U.S. Environmental Protection Agency
Office of Waste Programs Enforcement
Contract No. 68-W9-0006

[redacted]

TES 9

Technical Enforcement Support at Hazardous Waste Sites Zone III Regions 5,6, and 7

PRC Environmental Management, Inc.

187A
ACL#s

RCRA FACILITY ASSESSMENT SAMPLING
HYDROCARBON RECYCLERS, INC.
WICHITA, KANSAS

TES IX

SAMPLING PLAN

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Region 7
Kansas City, Kansas 66101

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REGIONAL SAMPLING PLAN APPROVAL

I have reviewed the attached sampling plan for Hydrocarbon Recyclers, Inc., Wichita, Kansas (EPA ID. No. KSD007246846), and find that it meets the criteria for technical accuracy for sampling and field analytical screening, implementation schedule, and sampling procedures.

APPROVAL:

PRC EMI Project Manager	1/6/92 Date
PRC EMI Quality Assurance Manager	Date
EPA Work Assignment Manager	1/6/92 Date
EPA Quality Assurance Manager	1/13/92 Date

1.0 INTRODUCTION

PRC Environmental Management, Inc. (PRC), received Work Assignment No. R07015 under Contract No. 68-W9-0006 (TES 9) from the U.S. Environmental Protection Agency (EPA) to conduct a Resource Conservation and Recovery Act (RCRA) Facility Assessment (RFA) at the Hydrocarbon Recyclers, Inc. (HRI) facility in Wichita, Kansas. PRC directed its TES 9 team firm, Black & Veatch Waste Science and Technology Corporation (BVWST) to complete the Preliminary Review (PR), and Visual Site Inspection (VSI) portion of the work assignment. The PRC team submitted a draft Preliminary Assessment Report for the facility on October 1, 1990. The report recommended a Sampling Visit (SV) be performed to determine if releases had occurred from various Solid Waste Management Units (SWMU) and Areas of Concern (AOC). This sampling plan outlines the project approach, work schedule, and methods to be employed during the SV.

1.1 SITE DESCRIPTION

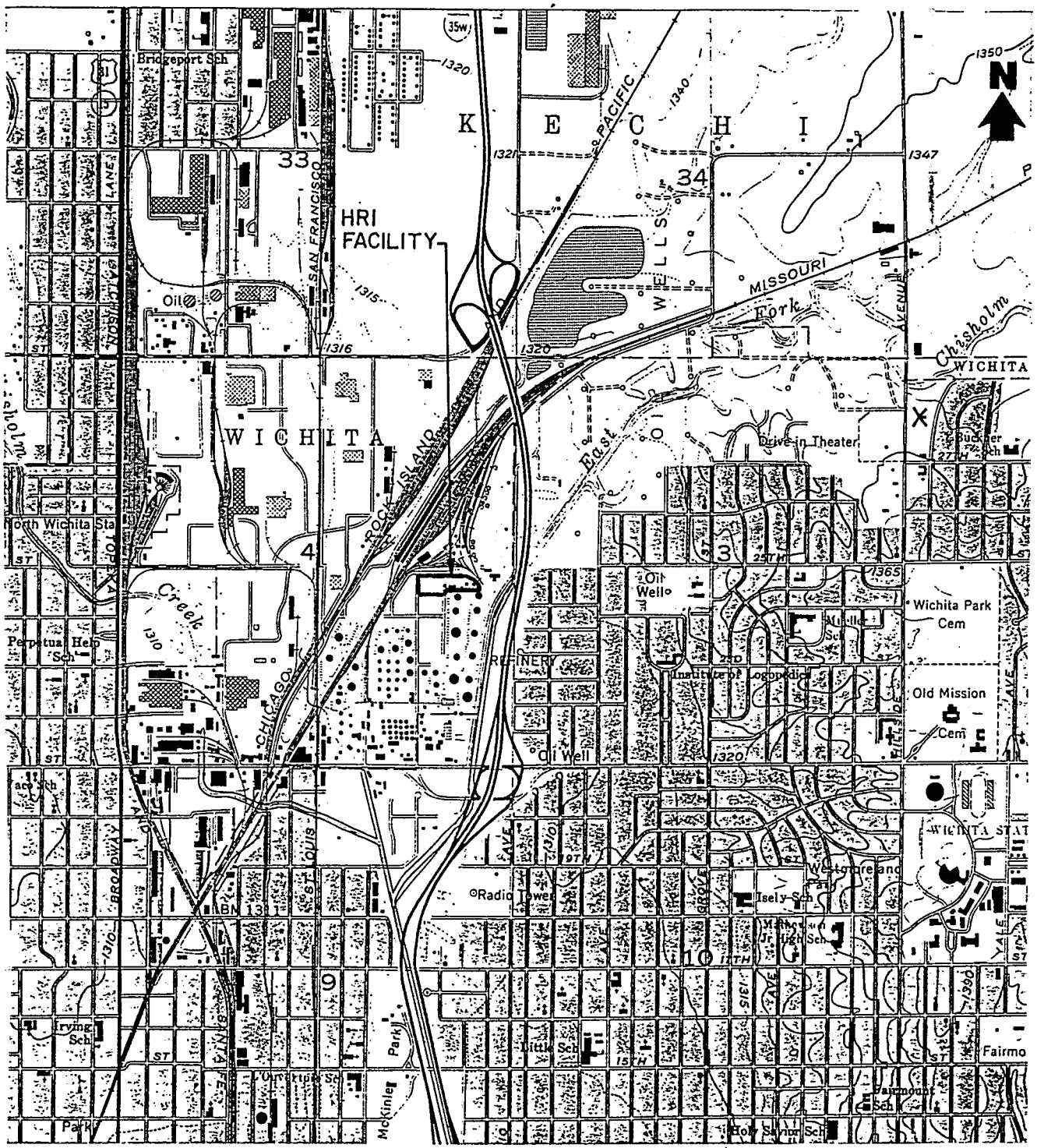
The HRI facility is located in the NE 1/4 of the SE 1/4 of Section 4, Township 27 South, Range 1 East from the Sixth Principal Meridian. The facility is located in a highly industrialized section of the City of Wichita, Kansas (Figure 1).

The facility contact is Chuck Trombold, General Manager. The facility address and telephone number is as follows:

Hydrocarbon Recyclers, Inc.
Chuck Trombold, General Manager
2549 North New York
Wichita, Kansas 67129
(316) 268-9490

1.2 SITE HISTORY

This facility has been the past location of the Enmar Paint Company, a distribution facility for industrial chemicals, and a receiving facility for spent solvents, electroplating sludges and other wastes. Currently the facility reclaims or recycles hazardous wastes. Hazardous wastes generated by this facility, or received wastes HRI is unable to reclaim or recycle, are shipped off-site to other treatment or disposal facilities.



SOURCE: U.S. GEOLOGICAL SURVEY, 7.5 MINUTE SERIES WITCHITA EAST QUADRANGLE, KANSAS, 1961.

HYDROCARBON RECYCLERS, INC.
WICHITA, KANSAS

FIGURE 1
SITE LOCATION MAP

PRC ENVIRONMENTAL MANAGEMENT, INC.

BVWST conducted a VSI at the HRI facility on June 19, 1990. The Preliminary Assessment Report was submitted to the EPA on October 1, 1990. BVWST identified 15 SWMUs and 8 AOC during the PR and VSI.

2.0 SAMPLING OBJECTIVE AND APPROACH

The objective of this sampling visit is to determine if a release of hazardous constituents from SWMUs or AOCs has occurred. A release will be considered any detected concentration of volatile organic compound, and or any concentration of semivolatile organic compounds or metals at or above the action levels defined in 40 CFR 264.521 Subpart S (Draft). The target analytes presented in the following sections were determined based on groundwater sample data from monitoring wells located on the facility property. Existing documentation on the primary wastes handled at this facility identifies volatile organic compounds, in the form of solvents, to be the compounds most likely to be identified in a release.

PRC utilizes a laboratory grade Shimadzu 14A gas chromatograph (GC) fitted with a photoionization detector (PID), a flame ionization detector (FID), and an electron capture detector (ECD). The signals from these detectors are processed in a Shimadzu Chromatopac two-channel integrator. Soil and water samples for volatile organic compound (VOC) analysis are analyzed via direct injection of a headspace sample. The headspace sample is prepared and extracted with a Tekmar 7000 Headspace Autosampler. The methodologies for all FAS procedures proposed in this sampling plan are attached in Appendices A, B, and C. Appendices A (VOC Analysis in Soils and Water Through Headspace Analysis) and B (PAH Analysis in Soils) are directly adapted from the Region 7 Field Investigation Team (FIT) Standard Operating Guidelines (SOG) for FAS. The FIT SOGs were modified to include the FAS equipment used by PRC. The SOG for metals analysis (Appendix C) has not been reviewed by the QADE. This SOG describes the procedures for analyzing water and soil via X-ray fluorescence using an HNu Model SEFA X-ray fluorescence analyzer (XRF).

Several of the targeted sampling locations were identified through interpretation of historical photographs of the facility (Figure 2). The uncertain location of potential contaminant sources in these areas will require a soil gas survey to locate potential release points of VOC. At each SWMU and AOC requiring a soil gas survey, PRC will obtain soil gas samples with a Geoprobe unit. These samples will be submitted to the PRC on-site mobile laboratory for FAS. These samples will be screened for VOCs. The design of the GC and the integrator will only allow two detectors to be run in series. For this FAS the ECD and FID will be run in series. Since the FID is a destructive analytical method the sample will be run past the ECD first. This configuration of detectors will allow detection of the VOCs previously detected in on-site

Figure 2
Sample Location Map

groundwater samples. The unit will be calibrated with 7 halogenated and non-halogenated VOC target compounds (Table 1). PRC will quantify levels of these target compounds in the soil, groundwater, and soil gas samples. The presence of other VOCs will be assessed on a qualitative basis, presence or absence. Specific detection limits are not relevant to this soil gas survey sampling. Soil gas is considered a semi-quantitative method for identifying VOC contamination sources. Areas exhibiting relatively higher concentrations of target compounds will be identified as potential sources. For reference, soil gas detection limits for the target compounds listed on Table 1 generally fall between the soil and water values.

At each target SWMU and AOC, PRC will obtain soil samples with a Geoprobe unit. These samples will be submitted to the PRC on-site mobile laboratory for FAS. The soil samples will first be screened for VOCs (Phase I). For this FAS the ECD and FID will be run in series. This configuration of detectors will allow detection of the primary VOCs detected in on-site groundwater samples, and the majority of compounds detected by Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) Method 8240. The unit will be calibrated with 7 halogenated and non-halogenated VOC target compounds (Table 1). PRC will quantify levels of these target compounds in the soil samples. The presence of other VOCs will be assessed on a qualitative basis, presence or absence.

Soil samples which either exhibit concentrations of the VOC target compounds above the detection limits, and or contain other VOCs qualitatively identified, will be submitted to the EPA Region 7 Laboratory for confirmatory analysis. These samples will be analyzed by SW-846 Method 8240. PRC will submit a minimum of 20% of the samples identified as potentially contaminated, for confirmatory analysis. PRC will also submit 10% of the samples exhibiting FAS non-detects for confirmatory analysis. This distribution of confirmatory analyses will allow documentation of a release as well as provide quality assurance/quality control (QA/QC data for the FAS data, per SOGs.

If VOCs are detected in less than 10% of the screening samples, PRC will go to phase II of the FAS approach. Splits of the VOC samples will be subjected to FAS for semivolatile analysis. The GC will be calibrated with three semivolatile target compounds (Table 2). The presence of other semi-volatiles can be assessed only on a qualitative basis, similarly to the phase I VOC screening.

Samples exhibiting concentrations of semivolatile target compounds above the detection limit, and or concentrations of other semi-volatiles qualitatively identified, will be submitted to the EPA Region Laboratory for confirmatory analysis. These samples will be analyzed by

TABLE 1

VOC TARGET COMPOUNDS AND FAS QUANTITATION LIMITS HYDROCARBON RECYCLERS, INC. WICHITA, KANSAS

Target Compound	Quantitation Limit1 (µg/kg for soils)	Quantitation Limit[1] (µg/L for water)
Trichloroethene	100	10
1,1,1 Trichloroethane	100	10
Carbon Tetrachloride	100	10
Tetrachloroethene	100	10
Toluene	100	10
Xylene	100	10
Benzene	100	10

Notes:

1 Specific quantitation limits are highly matrix dependent. These quantitation limits are provided for guidance and may not always be achievable. More specific limits will be provided during the QA/QC of the FAS data produced from this sampling.

SW-846 Method 8270. Method 8270 is being requested due to the uncertainty associated with potential semi-volatile organics potentially present in on-site soils. PRC will submit a minimum of 20% of the samples identified as potentially contaminated, for confirmatory analysis. PRC will also submit 10% of the samples exhibiting FAS non-detects for confirmatory analysis. This distribution of confirmatory analyses will allow documentation of a release as well as provide quality assurance/quality control (QA/QC) data for the FAS data, per SOGs.

If both VOCs and semi-volatiles are detected in less than 10% of the samples collected, PRC will screen the samples for metals with an XRF. This will be considered phase III of the FAS sampling at this facility. The target compound list for metals is found in Table 3.

Samples exhibiting a metals concentration greater the action levels identified in 40 CFR 265.521 Subpart S will be submitted to the EPA Region 7 Laboratory for confirmatory analysis. These samples will be analyzed by SW-846 Method 6010 and 7471. PRC will submit a minimum of 20% of the samples identified as potentially contaminated, for confirmatory analysis. PRC will also submit 10% of the samples exhibiting FAS non-detects for confirmatory analysis. This distribution of confirmatory analyses will allow documentation of a release as well as provide QA/QC data for the FAS data, per SOGs.

A high potential exists for release detection at the Former Drum Processing Area and the Non-regulated Waste Storage Area (Figure 2). Since these general areas are within buildings, making soil sampling impractical under this scope of work, a temporary groundwater monitoring system will be installed. The temporary monitoring wells that comprise this groundwater monitoring system will be constructed of 1-inch diameter hollow carbon steel pipe. This pipe has an inside diameter of 0.5-inches. The temporary monitoring wells will terminate with 2-feet of vertically slotted well screen. The slots have nominal width of 0.02-inches. These temporary monitoring wells will be installed with the Geoprobe unit. The top of the screens will be set approximately 1-foot below the top of the water table. Water table elevations will be determined through groundwater depth measurements from existing on-site monitoring wells. The water samples collected from the temporary monitoring wells will be subjected to the same FAS and confirmatory analysis plan as defined above for the soil samples.

The procedures outlined in SW-846 will be used to analyze all samples submitted to the EPA Region 7 Laboratory for verification. Samples collected for verification, including appropriate QA samples, will be analyzed for VOC (Method 8240), semi-volatiles (Method 8270), metals (6010), and mercury (Method 7470 and 7471). If phase I FAS provides greater than 10% detects for VOC, only Method 8240 will be run on confirmatory samples. If phase II FAS is

TABLE 2

SEMIVOLATILE TARGET COMPOUNDS AND FAS QUANTITATION LIMITS HYDROCARBON RECYCLERS, INC. WICHITA, KANSAS

Target Compound	Quantitation Limit[1] (µg/kg for soils)	Quantitation Limit[1] (µg/L for water)
Naphthalene	1,000	20
Benzo (a) pyrene	1,000	20
Ideno (1,2,3-cd) pyrene	1,000	20

Notes:

1 Specific quantitation limits are highly matrix dependent. These quantitation limits are provided for guidance and may not always be achievable. More specific limits will be provided during the QA/QC of the FAS data produced from this sampling.

TABLE 3

METAL TARGET COMPOUNDS AND FAS QUANTITATION LIMITS HYDROCARBON RECYCLERS, INC. WICHITA, KANSAS

Target Compound	Quantitation Limit[1] (mg/kg for soils)
Arsenic	50
Barium	50
Cadmium	50
Cobalt	50
Lead	50
Chromium	200
Mercury	50

Notes:

1 Specific quantitation limits are highly matrix dependent. These quantitation limits are provided for guidance and may not always be achievable. More specific limits will be provided during the QA/QC of the FAS data produced from this sampling. Quantitation limits for FAS for metals in water have not been defined at this time. This data will be back-calculated based on calibration standards and confirmatory analytical data.

used, Methods 8240 and 8270 will be run on confirmatory samples. If phase III FAS is utilized, confirmatory samples will be analyzed by Methods 8240, 8270, 6010, and 7040/7041. 7470/7471

The data quality objectives (DQO) for this sampling and screening effort will consider accuracy and completeness of analytical data. The required method detection levels will also be specified.

The accuracy of this sampling event will be evaluated by the FAS laboratory and the formal analytical laboratory. This evaluation will be based on standard spike recoveries. Spike recovery limits defined in the FAS SOGs and SW-846 will be used to assess accuracy.

Completeness of the analytical data will be determined by dividing the number of measurements judged valid by the total number of samples collected. The small number of samples being collected during this sampling event dictate that the data analyses have a 100 percent degree of completeness. This hold for both the FAS and formal analytical laboratory analyses.

FAS practical quantitation limits (PQL) are defined in the attached SOGs. These PQLs will be considered adequate for this FAS event. Standard SW-846 method detection levels (MDL) are requested for the confirmatory analyses (Table 4). These MDLs are considered adequate due to the lack of analytical data regarding soil contamination at this site.

3.0 SAMPLING APPROACH

This section will present the sampling design and rationale, proposed sampling team, schedule of activities, and the areas to be sampled.

3.1 SAMPLING DESIGN AND RATIONALE

Soil Gas Sampling

PRC proposes to conduct soil gas sampling in an area around the Concrete Vault, Open Area North of Building I, and the drainage trench just south of the Concrete Vault, and in the area around the Open Area Along the South West Corner (Figure 2). These areas were identified as potential release areas through examination of historical facility photographs. The soil gas surveys in these areas will be conducted in a grid pattern. The size of the grids depends on the total area to be covered. Since no scale drawing of the areas was available at the time this plan was prepared, grid size will be determined on-site. It is the general practice to start with a large

grid size and reduce the grid spacing, after the initial survey, in areas requiring finer definition. PRC anticipates a total of 30 soil gas samples will be collected from both areas.

Available information indicates that the water table should exist at approximately 15-feet below grade. Soil gas samples must be collected above the water table, preferably above the capillary fringe of the water table. Coarse textured materials allow the most effective soil gas sampling. Information on local soils suggests that the primary coarse textured horizon (above the water table), in the area around the site, exists at 5 to 10 feet below grade. Based on this information soil gas samples will be collected at 6-feet below grade. This shallow depth will also increase the potential detection of surface VOCs releases. If the soil texture does not allow the collection of soil gas samples at this depth, deeper attempts at collection will be made until a sample can be collected or the water table is reached. If the water table is reached first, an attempt will be made to collect shallower soil gas samples.

Soil gas samples will be collected through hollow steel pipe or polyethylene tubing. A vacuum will be used to purge and sample. Glass bulbs or disposable Tedlar bags will be used to contain the samples.

A 1-inch diameter carbon steel pipe fitted with an expendable carbon steel drive point will be driven to the sampling depth by the Geoprobe unit. The pipe will then be retracted approximately 6-inches. The expendable drive point will remain at the hole bottom, creating a 1-inch diameter by 6-inch long void under the steel rod. The steel rod is hollow (0.5-inch diameter). The gas sample can be extracted directly through the steel rod or through a polyethylene tube which can be attached via an air-tight seal to the rod bottom. If the sample is collected directly through the steel rod all threaded joints must be sealed using Teflon tape. Prior to sample collection 3-pipe volumes of air must be purged from the steel pipe or polyethylene tubing. This will remove any ambient air which may have been trapped in the sampling system. After purging the pipe or tubing the sample is collected directly into a reusable 250 mL glass sample bulb, or into a 500 mL disposable Tedlar bag. The samples will be delivered to the PRC mobile laboratory for FAS. The analysis will follow the methods described in appendix A except that the soil gas sample will be directly injected into the GC, no headspace sampling is necessary. The holding time for soil gas samples will not exceed 24-hours.

Soil Sampling

PRC proposes to collect soil samples at seven SWMUs/AOCs. The SWMU and AOC areas were identified in the RFA as potential areas of release, and by EPA representatives. If additional areas are sampled, the rationale for this alteration will be recorded in the project logbook and incorporated into the trip report. Since PRC has not been on site, specific sample

TABLE 4

SW-846
MAXIMUM ANALYTICAL DETECTION LIMITS FOR TARGET COMPOUNDS
HYDROCARBON RECYCLERS, INC.
WICHITA, KANSAS.

Target Compound	Method Detection Limit[1] (mg/kg for soils)	Method Detection Limit[1] (mg/L for water)
Trichloroethene	5	5
Carbon Tetrachloride	5	5
1,1 Trichloroethane	5	5
Tetrachloroethene	5	5
Toluene	5	5
Xylenes	5	5
Benzene	5	5
Naphthalene	660	10
Benzo (a) pyrene	660	10
Ideno (1,2,3-cd) pyrene	660	10
Arsenic	53	53
Barium	2	2
Chromium	7	7
Cobalt	7	7
Lead	42	42
Mercury	0.2	0.2

Note:

1 These method detection levels are based on standard SW-846 methodologies. These levels are expressed as µg/kg for soils and mg/l for extract, water.

locations, descriptions, or detailed discussions of sampling rationale will not be included in this section.

PRC will collect soil samples at two points in or around each targeted SWMU/AOC location. The SWMU and AOC sample locations will be determined on site by interpretation of soil gas data (where applicable), the evidence of staining, drainageways, or elevated readings with health and safety monitoring equipment.

PRC proposes to collect soil samples from the 0 to 12-inch depth interval and the 18 to 30-inch depth interval at each sample location. The shallow depth is intended to screen for the presence of surface released waste. The deeper sample will also be used to identify a surface soil release, however, the greater depth is intended to allow detection of VOCs which may have been volatilized from the upper soil horizons during to summer heating.

The samples will be collected with a 1.75 inch outside diameter thin-wall sampler driven to the sampling depth with the Geoprobe. Samples will be extruded into a stainless steel bowl and packaged in appropriate sample containers. At each sample point sufficient sample material will collected for FAS VOC, semi-volatile, and metals analysis (approximately 40 grams for each analysis), and formal laboratory analysis for VOCs, semi-volatiles, and metals. PRC will package VOC samples first, attempting to disturb the sample material as little as possible to prevent volatilization of potential contaminants. VOC sample containers will be filled with aliquots from the sample core. Void space in the sample container will be reduced through compaction of the sample with a wooden dowel-rod. The remaining sample material will be homogenized and placed in the appropriate sample containers. PRC will attempt to contact Ms. Nicole Roblez, EPA Region 7 Laboratory, if additional samples are to be submitted.

Groundwater Sampling

Groundwater samples will be collected from seven temporary monitoring well installations (Figure 2). No well development will be attempted for these monitoring wells unless metals samples are deemed necessary. If well development is needed to clarify the production water, prior to sampling, development will be accomplished by over pumping the well until the pH, conductivity and temperature readings stabilize. Readings will be considered stabilized if they do not vary by over 10 percent during three consecutive readings. The samples will be collected within 24-hours of well installation and thus no pre-sample purging of stagnant water is necessary. If no purging is required, one replicate sample will be collected from the well exhibiting the greatest contamination. This replicate will be collected after purging. This will allow a preliminary check of the no-purge rationale. If wells are sampled more than 24-hours

after installation they will be purged of three well volumes, and sampled within 24-hours of the purging event.

The VOC samples will be collected with a disposable polyethylene thieving tube, and other samples will be collected with a vacuum trap system. The samples for VOC analysis will be collected first, followed by the semi-volatiles samples, and the metals samples. All water samples will be placed on ice, in coolers, within 15-minutes of collection and preservation. The metals samples will require the addition of HNO_3 to lower their pH to <2.

If any proposed sample areas are under engineered containment structures at the time of sampling, no attempt will be made to sample directly under the containment. Samples in these areas will be collected adjacent to the containment in areas potentially affected by releases. These areas would include stained soils, down gradient locations, and areas near cracked or breached containment.

The following SWMUs and AOC are recommended for sampling (Figure 2):

Former Drum Processing Area

The former drum processing area was used to filter and blend spent solvents. This area is recommended for sampling because past compliance evaluation inspections noted the presence of containers that appeared to be leaking. A slight oil sheen was also observed in rainwater runoff from the former drum processing area. This area will be the target of the limited groundwater sampling effort.

Non-Regulated Waste Storage Area

The non-regulated waste storage area is used for the storage of non-regulated wastes and empty containers. This area is recommended for sampling because some spillage has occurred in this area and stained concrete was observed during the VSI. A large portion of the area does not have secondary containment. This area will be the target of the limited groundwater sampling effort.

Drum Crusher

Drums that are not sold for reconditioning, or are not reused, are crushed in this unit. The area containing the drum crusher and the adjacent gravel area is recommended for sampling

because no containment is present to prevent spillage or runoff. This area will be targeted for soil sampling only.

Other Area

Examination of historical photographs of this site identified this area to be an outdoor drum storage area. Based on the limited information regarding this area it is considered to have a moderate release potential. This area is slated for soil sampling only.

Drainage Out of the Concrete Vault Area

This area was the location of a hand dug trench used to drain the Concrete Vault Area and the Open Area North of Building I. If releases occurred in these two areas it is possible that the releases affected this drainage pathway. This area is considered to have a moderate release potential. This area will be included in the soil gas survey and the soil sampling effort.

Dry Solids Gondola

This unit is used to store dry solid waste removed from waste drums. Release of wastes during the loading of the gondola is possible. The lack of secondary containment around this unit increases the potential for release. Only soil samples will be collected in this area.

Open Area Along Southwest Corner

This area has been the storage location for empty drums, drums containing waste, and old process units. There is no reported containment in this area. The potential for release in this area is considered moderate. This area will be part of the soil gas and soil sampling effort.

Concrete Vault

This open concrete vault was used to contain once-through cooling water for a solvent distillation process. The walls of this vault have been etched by some material and exhibit vertical fracturing. The vault is open and thus receives precipitation. This water infiltrates into the surrounding soil through cracks in the vault. Based on the physical condition of the vault, and it being open to precipitation, this unit is considered to have a high potential for release. This area will be included in the soil gas and soil sampling effort.

Open Area North of Building I

This area was used for the storage of both virgin solvents in above ground tanks, and drummed waste. This area has no secondary containment. The RFA reports that some of this area is situated on open ground (no concrete cover). This area is considered to have a moderate potential for release. This area will be included in the soil gas and soil sampling effort.

3.2 SAMPLING TEAM

The PRC sampling team is listed below. All PRC field personnel participate in a medical monitoring program and have undergone the required training specified in 29 CFR 1910.

Designation	Name/Title
Team Leader/Sampler	Eric Hess, Soil Scientist
Safety Officer/FAS Leader	Wes Mccall, Geochemist
FAS Chemist	Brad Helland, Chemist
Geoprobe Operator	Keith Brown, Environmental Scientist

3.3 SCHEDULE OF SAMPLING ACTIVITIES

The sampling and FAS activities be conducted during the week of January 6, 1992. On-site activities should take no more than four ten hour days. The projected sample delivery date, to the Region 7 EPA Laboratory is January 13, 1992.

A total of 28 soil samples will be collected for FAS analysis (Table 5). Approximately 25% (8) of these will be submitted for confirmatory analysis: 7 environmental samples and 1 duplicate. A total of 10 water samples will be collected for FAS analysis (Table 5). Approximately 6 samples will be submitted for confirmatory analysis: 4 environmental samples, 1 duplicate sample, and 1 rinsate sample. In addition, one water trip blank, and one soil trip blank will be submitted for formal analysis to provide QA/QC for this sampling event.

3.4 SAMPLE COLLECTION PROCEDURES

The PRC sampling team will collect FAS and formal laboratory samples during this sampling activity. During this sampling effort, the PRC team will collect and split samples according to PRC and EPA Region 7 standard operating procedures (SOP), and FAS SOGs. The SOPs applicable to this effort are as follows:

TABLE 5

SAMPLE SUMMARY[1]
SAMPLE SERIES: UNASSIGNED
HYDROCARBON RECYCLERS INCORPORATED
WICHITA, KANSAS

Sample Location	Samples	No. of Matrix	Analysis	Containers/Sample	Preservatives
SWMU's and AOC's	28	Soil	VOC, BNA and Metals	2-40ML Vials 2-8oz Jars	None
Groundwater	7	Water	VOC, BNA, and Metals	2-40mL vials 1-80oz Jug 1-1 L Cubi	Ice Ice Ice,HNO_3
Duplicates	3	Soil	VOC, BNA, and Metals	2-40mL Vials 2-8oz Jars	None
Duplicates	1	Water	VOC, BNA, and Metals	2-40mL vials 1-80oz Jug 1-1 L Cubi	Ice Ice Ice,HNO_3
Trip Blank	1	Water	VOC	2-40mL vials 1-1 L Cubi	Ice Ice,HNO_3
Trip Blank	1	Soil	VOC	2-40mL Vials	None
Rinsate	1	Water	VOC, BNA, and Metals	2-40mL vials 1-80oz Jug 1-1 L Cubi	Ice Ice Ice,HNO_3

Notes:

1 A maximum of 25% of these samples will be submitted to EPA for formal analysis. BNA Base-neutral-acids (semi volatiles)

- **PRC SOPs**
  - No. 5 Soil Sampling
  - No. 17 Sample Collection Container Requirements - Section 2.0
  - No. 18 Sample Custody - Sections 2.1 to 2.4
  - No. 19 Sample Packaging and Shipment - Sections 1.3 to 2.4
- **EPA SOPs**
  - No. 2130.2A Field Chain-of-Custody for Environmental Samples - Approved 5-22-89
  - No. 2130.3A Identification, Documentation, and Tracking of Samples - Approved 10-11-89
  - No. 2130.4A Sample Containers - Approved 12-07-90

PRC will attempt to leave its investigation-derived wastes (IDW) on-site pending sample analysis. If the facility does not permit this, PRC will remove the waste to a permitted storage facility. This action could greatly increase the cost of this task, if the EPA Region 7 laboratory will not store the IDW. The determination of the hazardous or nonhazardous nature of the IDW will be based in the formal laboratory data generated from this sampling.

IDW will be handled in accordance with the proposed IDW Disposal Strategy outlined in the EPA IDW Management Guidance Manual - Second Draft, May 25, 1990. Only material that has come into contact with potentially contaminated material will be treated as IDW. Contamination avoidance practices will significantly reduce the volume of IDW. All other wastes will be treated as standard household-type waste.

4.0 FIELD QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Field QA/QC will be provided by implementing the SOPs and guidance documents listed in Section 3.4 of this work plan, as well as PRC's draft TES 9 Quality Assurance Program Plan (QAPP) for Region 7. Any deviations from these guidance documents, SOGs, or SOPs will be thoroughly documented in the field notebook.

4.1 FIELD DOCUMENTATION

Field documentation will include field notebooks, photographs, field data sheets, FAS sample logs, FAS chromatographs, and chain-of-custody forms. The team leader will be responsible for maintaining all field documentation. Field notes will be kept in a bound notebook. Each page will be sequentially numbered and labeled with the project name and number. Completed pages will be signed and dated by the individual responsible for the entries. Errors will have one line drawn through them and this line will be initialed and dated.

All photographs will be logged in the field notebook. These entries will include the time, date, direction, subject, witnesses, and the identity of the photographer. Specific notes regarding samples will be written on the sample field sheets, as well as in the field notebook. Field sheets generated by the Region 7 EPA Environmental Services Division will be completed as each sample is collected.

4.2 FIELD DECONTAMINATION

Disposable clothing or sampling equipment coming into contact with potentially contaminated material will be double-bagged and handled as IDW. Materials not coming into contact with potentially contaminated material will be disposed of in the local sanitary landfill.

Health and safety monitoring equipment will be bagged to prevent instrument contamination. The only open areas on the monitoring equipment will be at sample entry points.

Non-disposable sampling equipment will be decontaminated through a Alconox and water scrubbing, followed by tap water rinse. If soil particles are not removed by this decontamination method a high pressure hot water cleaning unit will be used for decontamination. All decontamination fluids will be containerized. At the conclusion of sampling, decontamination fluids will be sampled for VOC, semi-volatiles, and metals analysis to determine the regulatory category of these wastes. The decontamination fluids will be drummed in appropriate containers and left on-site pending analysis. If these materials require transport and or disposal off-site, additional funding will be needed for this work assignment.

4.3 QA/QC SAMPLES

The following types of QA/QC samples will be collected during the closure sampling oversight and submitted with environmental samples:

- Duplicate Sample
  - This sample will be used to evaluate the precision (reproducibility) of sample collection, matrix homogeneity, processing, and analysis. This sample will be collected from the most contaminated soil and groundwater location.
- Replicate Sample
  - This sample will be used to evaluate the hypothesis that purging the temporary monitoring wells prior to 24 hours after installation affects the sample integrity. This one groundwater sample will be collected after the duplicate is collected from the most contaminated well, and after the well is purged according to the procedures described in Section 3.1.
- Rinsate Sample
  - This sample will be used to evaluate the quality of the decontamination procedures and the chemical composition of the virgin decontamination water. This sample will be collected by pouring unused decontamination water over sampling material that has been decontaminated. An attempt will be made to collect this sample after decontaminating equipment used to collect a contaminated sample. This will be based on health and safety monitoring equipment measurements.
- Trip Blank
  - These samples are intended to evaluate contamination problems with shipping, packaging, and sample container preparation. These samples are typically reserved for QA/QC for volatile organics sampling.

4.4 SAMPLE CONTAINERIZATION, LABELING, AND PRESERVATION

The containerization and packaging of samples are described in Section 3.4 of this work plan, and in PRC SOP, no. 17, 18, and 19, and EPA Region 7 SOP no. 2130.2A, 3A, 4A, and 5A. Samples will be labeled in accordance with the draft PRC Region 7 TES 9 QAPP. The appropriate EPA sample tags and field sheets, as provided by the EPA Region 7 Laboratory, will be filled out as each sample is collected.

4.5 CHAIN OF CUSTODY AND SAMPLE TRANSPORT

A legal chain of custody will be maintained for sample bottles and samples at all times during the implementation of this work plan. The specifics of this task are outlined in PRC SOP no. 18 and 19, PRC FAS SOGs, and EPA Region 7 SOP no. 2130.2A. Standard Region 7 chain of custody forms will be used. All samples slated for confirmatory analysis will be sampler-conveyed to the Region 7 EPA Laboratory for analysis.

5.0 HEALTH AND SAFETY CONSIDERATIONS

PRC will follow the health and safety criteria described in the TES 9 Health and Safety plan developed for this site. This plan will be kept of file in the PRC project file. All PRC employees working on this site will comply with the requirements set forth in 29 CFR 1910.

6.0 LABORATORY AND QA/QC PROCEDURES

FAS QA/QC procedures are described in the attached SOGs. The formal laboratory analysis will observe the QA/QC procedures for inorganics analysis are defined under EPA SOPs in Section 3000 (Analytical Methods). Data packages from the FAS will be analyzed by PRC chemists, and the data packages from the formal analysis will be reviewed by EPA Region 7 Laboratory personnel.

7.0 PERFORMANCE AND SYSTEM AUDITS/CORRECTIVE ACTION

PRC has a draft QAPP, which includes performance audits, system audits, and corrective actions. Laboratory performance and system audits of the EPA Region 7 Laboratory are routinely carried out by EPA. This section addresses performance audits, system audits, and corrective actions of the field sampling activities conducted by PRC.

7.1 PERFORMANCE AUDITS

Performance audits are quantitative reviews of field activity. Performance audits include checks on sampling equipment, volume measurements, and analysis of QC samples. Performance audits are routinely carried out for each field operation undertaken by PRC personnel and are designed specifically for the particular field activities being conducted.

7.2 SYSTEM AUDITS

System audits are qualitative reviews of project activity. PRC initiates quarterly internal system audits to determine if the TES 9 procedures are being followed. The field equipment manager and work assignment manager routinely conduct system audits of field calibration logs and field notebooks to determine adherence to field SOPs.

7.3 CORRECTIVE ACTION

Corrective action will be required if the performance or system audits dictate. The decision criteria for corrective action are defined in both PRC's and EPA's SOPs or specifically outlined in the sampling plan. The implementation of field work may necessitate corrective action based solely on site-specific conditions. This type of corrective action, if necessary, will be defined and logged in the field notebook, including the rationale for corrective action and the rationale behind the specific corrective action that has been selected. Corrective action includes quantifying the types of errors, adjusting or qualifying field values, or instituting procedural changes.

APPENDIX A

STANDARD OPERATING GUIDELINES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOILS THROUGH HEADSPACE SAMPLING

DRAFT

FASP STANDARD OPERATING GUIDELINE

Analysis of Volatile Organic
Compounds in Soil/Sediment, Water and Air/Soil Gas
by the Automated Headspace Gas Chromatograph External Standard Method

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1.0 INTRODUCTION

This document contains a standard operating guideline (SOG) for performing volatile organic compound (VOC) analysis of soil/sediment, water, and air/soil gas samples using automated headspace technology in conjunction with a gas chromatograph (GC).

1.1 PURPOSE

This Field Analytical Support Project (FASP) method is proposed for use in determining the relative concentrations of various VOCs in soil/sediment, water, and air/soil gas samples using automated headspace technology and GC analysis.

1.2 USER RESTRICTIONS

The method should be used only by trained analysts under the supervision of an experienced chemist.

1.3 COMPOUNDS IDENTIFIED

Tables 1 through 1 list the compounds that may be determined by this method and approximate method quantitation limits. The method yields tentative identification and estimated relative quantitation of these compounds. Report values are on an "as received" basis -- no dry weights are used.

1.4 VERIFICATION

The primary objective of FASP is to provide analytical data in a timely manner for guidance of ongoing work in the field. Identification of specific or probable target compounds and prior knowledge regarding potential matrix interferences are prerequisites to successful use of FASP. FASP is not equivalent to or a replacement for Contract Laboratory Program (CLP) analyses. Verification of data through the CLP, encompassing the range of sample concentrations, is recommended.

TABLE 1

FASP TARGET COMPOUND LIST (FTCL) AND FASP QUANTITATION LIMITS (FQL) FOR VOCs IN SOIL/SEDIMENT

Volatile Organic Compound	CAS Registry Number	Quantitation Limits[a] Soil/Sediment (µg/kg)
Benzene	71-43-2	100
Bromodichloromethane	75-25-4	100
Bromomethane (Methyl Bromide)	74-83-9	100
Chlorobenzene	108-90-7	100
(2-Chloroethoxy)ethene (2-Chloroethyl Vinyl Ether)	110-75-8	100
Chloroethylene (Vinyl Chloride)	75-01-4	100
Carbon Tetrachloride	56-23-5	100
Dibromochloromethane	124-48-1	100
1,1-Dichloroethane (Ethylidene Chloride)	75-34-3	100
1,2-Dichloroethane (Ethylene Dichloride)	107-06-2	100
1,1-Dichloroethene (Vinylidene Chloride)	75-35-4	100
trans-1,2-Dichloroethene (Acetylene Dichloride)	540-59-0	100
Dichloromethane (Methylene Chloride)	75-09-2	100
1,2-Dichloropropane (Propylene Dichloride)	78-87-5	100
1,3-Dichloropropene (Dichloropropylene)	542-75-6	100
o,m,p-Dimethylbenzene (Xylenes)	1330-20-7	100
Ethylbenzene	100-41-4	100
Methylbenzene (Toluene)	108-88-3	100
2-Propenal (Acrolein, Acrylaldehyde)	107-02-8	100
2-Propenenitrile (Acrylonitrile)	107-13-1	100
1,1,2,2-Tetrachloroethane	79-34-5	100
Tetrachloroethene (Tetrachloroethylene)	127-18-4	100
Tribromoethane (Bromoform)	75-25-2	100
1,1,1-Trichloroethane (Methyl Chloroform)	71-55-6	100
1,1,2-Trichloroethane (Vinyl Trichloride)	79-00-5	100
Trichloroethene (Trichloroethylene)	79-01-6	100
Trichlorofluoromethane	75-69-4	100
Trichloromethane (Chloroform)	67-66-3	100

Notes:

Specific quantitation limits are highly matrix dependent. These quantitation limits are provided for guidance and may not always be achievable. More specific limits will be provided in revised FASP SOGs.

[a] Quantitation limits are calculated on an as-received basis.

TABLE 2

FASP TARGET COMPOUND LIST (FTCL) AND FASP QUANTITATION LIMITS (FQL) FOR VOCs IN WATER

Volatile Organic Compound	CAS Registry Number	Quantitation Limits[a] Soil/Sediment (µg/kg)
Benzene	71-43-2	10
Bromodichloromethane	75-25-4	10
Bromomethane (Methyl Bromide)	74-83-9	10
Chlorobenzene	108-90-7	10
(2-Chloroethoxy)ethene (2-Chloroethyl Vinyl Ether)	110-75-8	10
Chloroethylene (Vinyl Chloride)	75-01-4	10
Carbon Tetrachloride	56-23-5	10
Dibromochloromethane	124-48-1	10
1,1-Dichloroethane (Ethylidene Chloride)	75-34-3	10
1,2-Dichloroethane (Ethylene Dichloride)	107-06-2	10
1,1-Dichloroethene (Vinylidene Chloride)	75-35-4	10
trans-1,2-Dichloroethene (Acetylene Dichloride)	540-59-0	10
Dichloromethane (Methylene Chloride)	75-09-2	10
1,2-Dichloropropane (Propylene Dichloride)	78-87-5	10
1,3-Dichloropropene (Dichloropropylene)	542-75-6	10
o,m,p-Dimethylbenzene (Xylenes)	1330-20-7	10
Ethylbenzene	100-41-4	10
Methylbenzene (Toluene)	108-88-3	10
2-Propenal (Acrolein, Acrylaldehyde)	107-02-8	10
2-Propenenitrile (Acrylonitrile)	107-13-1	10
1,1,2,2-Tetrachloroethane	79-34-5	10
Tetrachloroethene (Tetrachloroethylene)	127-18-4	10
Tribromoethane (Bromoform)	75-25-2	10
1,1,1-Trichloroethane (Methyl Chloroform)	71-55-6	10
1,1,2-Trichloroethane (Vinyl Trichloride)	79-00-5	10
Trichloroethene (Trichloroethylene)	79-01-6	10
Trichlorofluoromethane	75-69-4	10
Trichloromethane (Chloroform)	67-66-3	10

Notes:

Specific quantitation limits are highly matrix dependent. These quantitation limits are provided for guidance and may not always be achievable. More specific limits will be provided in revised FASP SOGs.

[a] Quantitation limits are calculated on an as-received basis.

TABLE 3

FASP TARGET COMPOUND LIST (FTCL) AND FASP QUANTITATION LIMITS (FQL) FOR VOCs IN SOIL GAS

Volatile Organic Compound	CAS Registry Number	Quantitation Limits[a] Soil/Sediment (µg/kg)
Benzene	71-43-2	10-100
Bromodichloromethane	75-25-4	10-100
Bromomethane (Methyl Bromide)	74-83-9	10-100
Chlorobenzene	108-90-7	10-100
(2-Chloroethoxy)ethene (2-Chloroethyl Vinyl Ether)	110-75-8	10-100
Chloroethylene (Vinyl Chloride)	75-01-4	10-100
Carbon Tetrachloride	56-23-5	10-100
Dibromochloromethane	124-48-1	10-100
1,1-Dichloroethane (Ethylidene Chloride)	75-34-3	10-100
1,2-Dichloroethane (Ethylene Dichloride)	107-06-2	10-100
1,1-Dichloroethene (Vinylidene Chloride)	75-35-4	10-100
trans-1,2-Dichloroethene (Acetylene Dichloride)	540-59-0	10-100
Dichloromethane (Methylene Chloride)	75-09-2	10-100
1,2-Dichloropropane (Propylene Dichloride)	78-87-5	10-100
1,3-Dichloropropene (Dichloropropylene)	542-75-6	10-100
o,m,p-Dimethylbenzene (Xylenes)	1330-20-7	10-100
Ethylbenzene	100-41-4	10-100
Methylbenzene (Toluene)	108-88-3	10-100
2-Propenal (Acrolein, Acrylaldehyde)	107-02-8	10-100
2-Propenenitrile (Acrylonitrile)	107-13-1	10-100
1,1,2,2-Tetrachloroethane	79-34-5	10-100
Tetrachloroethene (Tetrachloroethylene)	127-18-4	10-100
Tribromoethane (Bromoform)	75-25-2	10-100
1,1,1-Trichloroethane (Methyl Chloroform)	71-55-6	10-100
1,1,2-Trichloroethane (Vinyl Trichloride)	79-00-5	10-100
Trichloroethene (Trichloroethylene)	79-01-6	10-100
Trichlorofluoromethane	75-69-4	10-100
Trichloromethane (Chloroform)	67-66-3	10-100

Notes:

Specific quantitation limits are highly matrix dependent. These quantitation limits are provided for guidance and may not always be achievable. More specific limits will be provided in revised FASP SOGs.

[a] Quantitation limits are calculated on an as-received basis.

1.5 LIMITATIONS

This FASP is intended only to generate screening data that can be used to direct ongoing field work, identify samples that need additional analysis, or determine relative concentrations of target analytes. The headspace technique assumes that for analytes which volatilize at the prescribed temperatures, the concentration of an analyte found in the headspace over the soil/sediment sample is either in equilibrium with the concentration of the analyte in the sample matrix or that the analyte is distributed in a well-defined manner between the headspace and the sample matrix. This assumption is usually valid. However, oily wastes, multi-phase samples, and concentrated samples may result in complex interferences which could prevent the assumed partitioning between the liquid and gas phases in the headspace vial. Thermal decomposition or reaction of target analytes in the sample matrix may also limit method accuracy, although empirical adjustments to analysis parameters can minimize or eliminate such problems.

2.0 SUMMARY OF METHOD

This section summarizes the FASP methods for analyzing VOCs in soil/sediment, water, and air/soil gas using automated headspace technology and GC analysis.

2.1 SOIL/SEDIMENT METHOD

A measured amount of soil/sediment sample is placed into a headspace vial. The headspace volume is made constant for all samples and standards. The containers are sealed and allowed to equilibrate at a constant temperature at or near the boiling point of the target analyte(s) in the headspace analyzer. A sample is withdrawn from the headspace and injected onto a temperature programmed gas chromatograph equipped with a packed or megaborous capillary column. Volatile organic compounds are detected with a photoionization detector (PID) and an electron capture detector (ECD) connected in series. Quantitation and identification are based on relative peak areas and relative retention times using the external standard method.

2.2 WATER METHOD

A measured amount of water sample is placed into a headspace vial. The headspace volume is made constant for all samples and standards. The containers are sealed and allowed to equilibrate at a constant temperature, usually near 80 °C, in the headspace sampler. A sample is withdrawn from the headspace and injected onto a temperature programmed gas chromatograph

equipped with a packed or megabore capillary column. Volatile organic compounds are detected using a photoionization detector (PID) and an electron capture detector (ECD) connected in series. Quantitation and identification are based on relative peak areas and relative retention times using the external standard method.

2.3 AIR/SOIL GAS METHOD

A soil gas sample is collected in a 1-L Tedlar bag or a gas sampling tube. A specific volume of gas is withdrawn from the Tedlar bag or sampling tube with a gas-tight syringe and directly injected onto a temperature programmed gas chromatograph equipped with a packed or megabore capillary column. Volatile organic compounds are detected with a PID and an ECD connected in series. Quantitation and identification are based on relative peak areas and relative retention times using the external standard method.

3.0 INTERFERENCES

There are many factors which may potentially cause interference when analyzing VOCs with this method. Impurities in the carrier gas, organic compounds out-gassing from the system's plumbing, and solvent vapors in the laboratory account for the majority of contamination problems which will interfere with the analytical results. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks.

3.1 SYSTEM PLUMBING AND GAS CONTAMINATION

The use of non-Teflon tubing, non-Teflon thread sealants, or flow controllers with rubber components should be avoided. Flow controllers and plumbing designed for analytical gas chromatography are recommended. A carrier gas purification system is also desirable to avoid oxygen and other trace gas contamination which may cause interference and column degradation.

3.2 SAMPLE CARRY-OVER

Contamination by carry-over can occur whenever high-level samples are analyzed. To reduce carry-over, any sampling syringe used must be rinsed with methanol or another organic solvent suitable for dissolving the sample matrix, dried in an oven, then stored in a desiccator between sample analyses. Whenever an unusually concentrated sample is encountered, it should

be followed by an analysis of the headspace over reagent water and/or analysis of the sampling syringe filled with reagent air to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or viscous compounds, it may be necessary to boil the sampling syringe with water for several minutes, rinse with methanol or another organic solvent suitable for dissolving the sample matrix, dry it in an oven at 105 °C, and store it in a desiccator between analyses. The headspace sampler and other parts of the system are also subject to contamination; therefore, frequent purging of the entire system may be required.

3.3 CROSS CONTAMINATION

Cross contamination from solvents could potentially interfere with analytical results. The laboratory where VOC analysis is performed should be completely free of solvents and the GC and headspace sampler should be swept with an ample volume of carrier gas between samples to minimize the possibility of cross contamination.

3.4 NON-IDEALLY DILUTE SOLUTIONS

Henry's Law states that the concentration of the volatile analyte in the headspace above the solution is proportional to the concentration of the analyte in solution. This proportionality, known as Henry's Constant, is temperature dependent under laboratory conditions. Henry's Law holds only for ideally dilute solutions. Ideally dilute solutions can be conveniently defined as solutions with less than 1 percent total dissolved species. In practice, the water solubility of the analyte being measured, which is typically on the order of 1000 µg/l to 10 g/l, rarely exceeds the limits of ideally dilute solutions. If necessary, the concentration can be reduced by diluting samples that contain quantities of analytes which exceed their water solubility limit. Caution in the interpretation of results for samples needing dilution should be exercised especially if free product is present in the original sample.

3.5 SPECIAL ANALYTICAL SERVICES TECHNIQUES

Interferences co-extracted from samples are matrix and site specific. It is possible that techniques used in either FASP or CLP Routine Analytical Services (RAS) methods may fail to eliminate interferences. Highly specialized CLP Special Analytical Services (SAS) techniques may be required to produce acceptable analytical results.

4.0 APPARATUS AND MATERIALS

This section describes the apparatus and materials required to conduct FASP analyses of VOCs in soil/sediment, water, and air/soil gas. The analytical systems and other associated equipment are discussed below.

4.1 ANALYTICAL SYSTEMS

The analytical system consists of three major components: the GC, the integrator, and the headspace sampler. Analysis of soil/sediment and water samples requires the use of all components. Analysis of air/soil gas does not require the use of the headspace sampler. The particular GC and headspace analyzer used are discussed below.

4.1.1 GAS CHROMATOGRAPH

This analytical system is complete with a temperature programmable GC suitable for direct injection. All necessary accessories, including injector and detector systems designed or modified to accept the appropriate analytical columns (packed or megabore), are included. This analytical system has a data-handling device attached to the detectors that is capable of retention time labeling, relative retention time analysis, and relative and absolute peak height and/or peak area measurement.

4.1.1.1 ANALYTICAL COLUMNS

The packed column specifications are: 1.8 m x 3 mm Inside Diameter (ID) glass column packed with 1 percent SP-1000 on Carbopack B (60/80 mesh) or equivalent. The capillary column specifications are: 30 m x 0.53 mm ID DB-624 fused silica megabore column (J&W Scientific) or equivalent.

4.1.1.2 DETECTORS

A PID with a 10.2 eV lamp and a auxiliary gas supply at the detector inlet is connected in series to an ECD.

4.1.1.3 GAS SUPPLY

The carrier gas and auxiliary gas is zero grade nitrogen (99.99% minimum purity, oxygen (O_2) 5 parts per million (ppm) maximum, total hydrocarbons (THC) 0.5 ppm maximum). All gases should pass through oxygen and/or hydrocarbon traps prior to the analytical system to prevent degradation of the column stationary phase and to prevent analytical interference.

4.1.2 HEADSPACE SAMPLER

Sample introduction is accomplished using a Tekmar 7000 headspace sampler or equivalent. This sampler is capable of automatically heating a group of samples to a constant temperature for a specified period of time. The Tekmar 7000 headspace sampler automatically withdraws a 3 ml sample from the headspace of the sample to be analyzed. A larger volume loop is available if additional sample is required. The sample carousel, sample loop, and transfer line inserted into the GC injector are heated, which minimizes sample carryover.

4.1.3 INTEGRATOR

Shimadzu C-R4A Chromatopac with a dual channel interface and hard disk drive for data storage or equivalent.

4.2 OTHER LABORATORY EQUIPMENT

Various other pieces of laboratory equipment are commonly used during sample preparation and analysis and are described below.

Micro-syringes: 10 µl, 25 µl, and larger.
Sample Syringes: 0.1 ml, 0.5 ml, 1.0 ml, gas tight with Teflon valve.
Volumetric Flasks: 10 ml, 50 ml, 100 ml with ground glass stoppers.
Vials: 1.8 ml for purgeable standards with Teflon-lined septa, and headspace vials with Teflon-lined septa and aluminum crimp caps, 22 ml or other appropriate size to fit headspace sampler.
Vortex Mixer: Fisher Scientific or equivalent for optional sample agitation.
Desiccator: Glass with appropriate desiccant.
Teflon Squeeze Bottles: 500 ml.

Headspace Vial Cap Crimper Pliers.

Drying Oven: To dry glassware and insure rapid sample turnaround.

Oxygen Traps: Supelpure-O-Trap and OM-1 indicating tube, or equivalent.

Leak Detector: Snoop brand liquid or equivalent for packed column operations or GOW-MAC gas leak detector, or equivalent for megabore capillary operations.

Chromatographic Data Stamps: Used to record instrument operating conditions.

Spatulas, Stainless Steel.

Top Loading Balance: ±0.1 g.

Micropipette: Oxford Benchmate or equivalent, continuous, 10-50 µl, 1-10 µl.

Gas Sample Tube or Tedlar Bag.

Refrigerator: 3 cubic ft for standard storage.

5.0 REAGENTS

Several solvents, gases, and solutions are used in conjunction with the FASP analytical method. The various reagents used are discussed below.

5.1 SOLVENTS

Solvents may be used for extraction prior to analysis. The solvents used with this method are:

- Propanol, GC grade.
- Methanol, GC grade.
- Ethyl Acetate, GC grade.

5.2 GASSES

Nitrogen is used as the carrier gas to move the sample through the GC column and the auxiliary gas in detectors. Zero grade (see 4.1.1.3) will be used in conjunction with an O_2 trap.

5.3 STOCK STANDARD SOLUTIONS

Stock standard solutions should be purchased in methanol as manufacturer certified solutions. These solutions will be used to prepare the external calibration standards for the GC.

5.4 EXTERNAL CALIBRATION STANDARDS

Calibration standards will be prepared at a minimum of three concentration levels for each target analyte. This is done immediately before analysis through volumetric dilution of stock standards with water. The lowest concentration standard will be approximately two times the FQL as listed in Tables 1 through 3. The remaining concentration levels will define the approximate working range of the GC: one standard at the upper linear range and the other midway between the highest and the lowest standard. All calibration standards must be stored at 4 °C in Teflon-sealed glass vials in the absence of light. Calibration standard solutions must be replaced weekly, or sooner if comparison with check standards indicates significant deviation.

5.5 CHECK STANDARDS

Check standards are calibration standards independently prepared by a chemist other than the calibration standard preparer, are used only to confirm external calibration standards, and are stored at 4 °C

5.6 MATRIX SPIKE SOLUTIONS

Matrix spike solutions will be prepared by dilution of stock standard solutions so that no more than 250 µl of spike solution are required to provide a sample spike level within FASP QC limits.

5.7 LABWARE CLEANING AND DECONTAMINATION SOLUTIONS

Lab glassware may be cleaned and decontaminated with Alkonox detergent solution followed by distilled water rinse. A base bath (Potassium Hydroxide in Ethanol) or an acid bath may be used to clean glassware resistant to normal cleaning. Clean glassware may be rapidly and effectively dried by rinsing with minute amounts of acetone and drying in an oven.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

The sample containers required, sample preservation methods, and sample handling procedures are discussed below.

6.1 SAMPLE COLLECTION

Specific containers are required for the various media analyzed using this method. Soil/sediment and water samples are collected in two 40-ml vials with Teflon-lined septa caps. Air/soil gas samples are collected in two one liter each Tedlar bags or in gas sample tubes. Actual sample volume required for analysis is approximately 5g of soil/sediment, 5 ml of water and 20 ml of air/soil gas. The additional volume is collected in case of container breakage or leakage.

6.2 SAMPLE PRESERVATION

All soil/sediment and water samples collected will be stored on ice until analysis. all air/soil gas samples will be stored in a cool dark place until analysis. All samples will be analyzed within approximately 24 hours of collection time.

6.3 SAMPLE HANDLING

Sample locations, sample numbers, time, and date will be recorded in a field log book at time of collection. Soil/sediment samples will be numbered beginning with S-001, ground-water samples will be number beginning with W-001, and air/soil gas samples will be numbered beginning with SG-001. Duplicate samples will be assigned a "D" suffix and field blanks will be assigned a "B" suffix.

A log will be kept as samples are turned over to the on-site laboratory. The field chemist will track the samples received to ensure all samples will be analyzed within the proper time limit.

7.0 CALIBRATION

Calibration of the GC is crucial to the analyses of all the environmental media to be sampled. Calibration will occur at various times throughout the project. The major types of calibration procedures are initial calibration, continuing calibration, and final calibration.

7.1 INITIAL CALIBRATION

After an experienced chromatographer has ensured that the entire chromatography system is functioning properly (conditions exist such that resolution, retention times, peak area reporting, and interpretation of chromatographic spectra are within acceptable quality control limits), the GC may be calibrated by the external standard technique (See 10.0). Using at least three calibration standards prepared as described in Section 5, initial calibration curves (relative response versus mass of standard injected) are generated for each analyte (see 10.1).

The percent relative standard deviation (%RSD, see 10.1) based on each volatile organic analyte's three calibration factors (CFs, see 10.1) is computed to determine the linearity of the curve. Unless otherwise specified, the %RSD must be $\leq$ 25 percent or the calibration is invalid and must be repeated. Any time the GC system is altered (e.g., new column, change in gas supply, change in oven temperature program, etc.), a new initial calibration curve must be established.

7.2 CONTINUING CALIBRATION

The GC system will be rechecked on a regular basis through the continuing calibration. The mid-range initial calibration standard is generally the most appropriate choice for continuing calibration validation. This single point analysis follows the same analytical procedures used in the initial calibration. Instrument response is used to compute the CF which is then compared to the mean initial CF and a relative percent difference (RPD, see 10.2) is calculated. Unless otherwise specified, the RPD for all analytes must be $\leq$ 25 percent for the continuing calibration to be considered valid, or the calibration must be repeated. A continuing calibration remains valid for a maximum of 24 hours providing the GC system remains unaltered during that time.

The continuing calibration is employed in all sample concentration quantitation calculations (see 10.4) for the period over which the calibration has been validated.

7.3 FINAL CALIBRATION

The continuing calibration must be repeated prior to the end of each 24-hour period in which samples are analyzed. The maximum allowable RPD between the initial calibration and final calibration factors for each target analyte is $\leq$ 50 percent. A final calibration which achieves $\leq$ 25 percent RPD for all target analytes may be used as an ongoing continuing calibration.

8.0 SAMPLE PREPARATION

Sample preparation is the process in which samples are modified from the time of collection to the actual time for analysis. The procedures used for preparing soil/sediment, water, and air/soil gas samples are discussed below.

8.1 SOIL/SEDIMENT SAMPLES

The sample preparation technique for VOCs in soils/sediment is as follows:

1) The appropriate amount of sample will be added to a headspace sample vial. All samples, standards, and QC samples must have consistent final volumes in order to allow for consistent headspace volume.

2) Immediately seal the headspace vial with a Teflon-coated septum and aluminum crimp cap using the headspace vial cap crimping pliers.

3) The vial will be placed in the headspace sampler, and equilibrated at the appropriate temperature (usually at least 30 minutes). NOTE: Samples, standards, and/or QC samples should be prepared as a group.

8.2 PREPARATION OF WATER SAMPLES

The sample preparation technique for VOCs in water is as follows:

1) The appropriate amount of sample will be added to a headspace sample vial. All samples standards, and QC samples must have consistent final volumes in order to allow for consistent headspace volume.

2) The headspace will be immediately sealed with a Teflon-coated septum and aluminum crimp cap or screw cap.

3) The vial will be placed in the headspace sampler and equilibrated at the appropriate temperature (usually at least 30 minutes). NOTE: Samples, standards, and/or QC samples should be prepared as a group.

8.3 PREPARATION OF AIR/SOIL GAS SAMPLES

No sample preparation is necessary for analysis of VOCs in soil gas; samples are directly injected onto the GC.

9.0 INSTRUMENTAL ANALYSIS

Conducting the analysis of multi-media environmental samples involves properly operating the headspace sampler and the GC. This includes operating at the proper temperature and gas pressure settings and programming of equipment parameters. Other procedures involved in sample analysis include adjusting the parameters for the chromatograms, identifying VOCs based on their retention times, and performing the proper analytical sequence, including external standard calibration.

9.1 INSTRUMENT PARAMETERS

Tables 4 and 5 exemplify acceptable operating conditions for the analytical system. Table 4 provides example parameters for the headspace sampler during the analysis of soil/sediment or water samples. The headspace sampler is not required during the analysis of air/soil gas samples. Table 5 provides examples of GC operating conditions for the analysis of all three environmental media. Other instruments, columns, and or chromatographic conditions may be employed only if FASP quality control criteria are met.

9.2 CHROMATOGRAMS

Chromatograms are the actual printed charts or electronic images which contain peaks representing the compounds detected. Generally, peak response will be >25 percent and <100 percent of full-scale deflection to allow ease of VOCs analysis.

The following information will be recorded on each chromatogram:

- Instrument and detector identification
- Column packing, coating, length, and I.D.
- Oven temperature/temperature program
- Injector/detector temperatures
- Gases and flow rates
- Site name
- Sample number
- Date and time
- GC operator initials

TABLE 4

EXAMPLE PARAMETERS FOR THE HEADSPACE SAMPLER

TEMPERATURE SETTINGS

Heating Block Temperature	50-100 °C
Valve Loop Temperature	≥100 °C

GAS PRESSURES AND SETTINGS - TEKMAR MODEL 7000

Gas Mode	Type of Gas	Tank Pressure (lbs)	Bar Setting
Carrier	Nitrogen	40	0.7
Auxiliary	Nitrogen	40	1.1

PROGRAMMING TIMING FOR VALVE OPERATION EVENTS

Command	Function/Activity
LOAD	LOAD SAMPLE VIAL INTO PLATTEN
SAMPLE EQUILIBRATE	SAMPLE VIAL HEATS AT SPECIFIED TEMPERATURE FOR SPECIFIED TIME
MIX	SAMPLE VIAL IS AGITATED AT SPECIFIED POWER FOR SPECIFIED TIME
STABILIZE	POST-MIXING STABILIZATION
PRESSURIZE	CARRIER GAS PRESSURIZES VIAL
PRESSURE EQUILIBRATE	SAMPLE MATRIX AND SAMPLE VAPORS EQUILIBRATE AT NEW PRESSURE
LOOP FILL	PRESSURIZED VIAL RELEASES VAPOR TO FILL 3 ML SAMPLE LOOP
LOOP EQUILIBRATE	VAPOR EQUILIBRATES TO LOOP TEMPERATURE
INJECT	SAMPLE VAPOR INJECTED ONTO GC

TABLE 5

EXAMPLE FASP TEMPERATURE PROGRAM GC OPERATING CONDITIONS

Headspace Sampler:	Tekmar 7000 Automatic Headspace Sampler with heated transfer line.
Instrument:	An analytical system complete with a temperature programmable GC and all required accessories including analytical columns, gases, and equipped with a PID Detector with a 10.2 eV lamp connected in series to an ECD.
Integrator:	Shimadzu C-R4A Chromatopac with a dual channel interface and hard disk drive for data storage.
Column:	J&W DB-624 fused silica megabore column, 30 m x 0.53 mm. I.D.
Carrier Gas:	Zero grade nitrogen, 10 ml/min.
Auxiliary Gas:	Zero grade nitrogen, 40 ml/min.
Column Oven:	Initial temperature: 50 °C Initial time: 4 mins Ramp rate: 8 °C/min Final temperature: 190 °C Final hold time: 4 mins
Injector Temperature:	150 °C
Detector Temperature:	PID: 200 °C ECD: 300 °C
GC Analysis Time:	30 mins
Sample Injection:	A 3 ml aliquot of the headspace gas is automatically injected into the GC via the heated transfer line. If greater sample quantity is desired, a larger volume sample loop may be employed.

9.3 VOC IDENTIFICATION

Qualitative identification of FTCL VOCs is based on both detector sensitivity and relative retention time compared to known external standards. For a compound which is detected on both the PID and ECD, the compound should be identified in both chromatograms for a positive identification to be made. Generally, individual peak relative retention time windows will be ≤ 5 percent for packed column analysis or ≤ 2 percent for megabore capillary columns. It may not be possible or practical to separate all volatile organic target compounds on a single column. In such cases, these target compounds will be denoted as the appropriate combination of VOCs.

9.4 ANALYTICAL SEQUENCE

A strict operating sequence will be followed throughout the project during the analysis of VOCs using this method. The analytical sequence to be followed is outlined below.

1) Perform an instrument blank.

2) Conduct the initial calibration.

3) Check standard solution and/or performance evaluation sample (if available).

4) Conduct continuing calibration; repeat within 24 hours of previous continuing calibration.

5) Run a system performance check sample (if available).

6) Perform an associated QC lot method blank.

7) Analyze twenty environmental samples and associated QC lot spike and duplicate.

8) Repeat sequence beginning at Step 5 until all sample analyses are completed or another continuing calibration is required.

9) Conduct the final calibration when all sample analyses are complete.

10.0 CALCULATIONS

Several calculations are required to determine calibration and sample quantitation. The procedures for carrying out these calculations are presented below.

10.1 INITIAL CALIBRATION

Initial calibration will be conducted after the entire chromatography system is set up and functioning. Calibration standards will be analyzed for each analyte. The area response of each analyte will be tabulated against mass of each analyte, and CFs for each analyte will be calculated according to the following equation:

$$CF = \frac{\text{Area of Peak}}{\text{Mass Injected (in micrograms)}}$$

Using the CF values, calculate the percent relative standard deviation (%RSD) for each analyte at all three calibration concentration using the equation below.

$$\% \text{ RSD} = \frac{SD}{\bar{S}} \times 100$$

where SD, the Standard Deviation is given by:

$$SD = (\Sigma(S_i - \bar{S})^2)^{1/2}(N-1)$$

where: S_i = individual CF (per analyte),

$\bar{S}$ = mean of initial three CFs(per analyte), and

N = number of calibration standards.

The %RSD must be ≤ 25.0 percent.

10.2 CONTINUING CALIBRATION

Continuing calibration will be performed by rechecking the GC system on a regular basis. Sample quantitation is based on analyte CFs calculated from continuing calibrations. Mid-range standards for all initial calibration target analytes will be analyzed at specified intervals (≤ 24 hours).

The maximum allowable relative percent difference (RPD) calculated using the equation below for each analyte is ≤ 25 percent.

$$RPD = \frac{abs(CF_I - CF_C)}{[(CF_I + CF_C)/2]} \times 100$$

where: abs indicates absolute value

CF_I = mean CF from the initial calibration for each analyte

CF_C = measured CF from the continuing calibration for the same analyte

10.3 FINAL CALIBRATION

The final calibration is obtained at the end of each 24-hour period in which samples are analyzed.

The maximum allowable RPD (see 10.2) between the mean initial calibration and final calibration factors for each target analyte is ≤ 50 percent. A final calibration which achieves ≤ 25 percent RPD may be used as an ongoing continuing calibration.

10.4 SAMPLE QUANTITATION

Identification and quantitation of FTCL VOCs should be based on the external standard method. A compound which is detected by both the PID and ECD should be quantified using the detector which gives the higher CF for that specific compound. The second detector should be used for confirmation of the presence of that compound.

External standard calibration is used for the calculation of analyte concentration. The concentration of each calibrated analyte may be determined by the following formula:

$$\text{Concentration } (\mu g/kg) \text{ (wet weight)} = \frac{(A_x)}{(W)(CF_c)}$$

where: A_x = area of the peak for the analyte in the sample.

W = weight (g) of sample injected.

CF_c = the calibration factor for the analyte to be measured.

Results are reported in micrograms per kilogram (µg/kg) without correction for blank or spike recovery.

Co-eluted compounds should be quantified and reported as the combination of the unseparated volatile organic analytes.

Sample chromatograms may not match identically with those of analytical standards. When positive identification is questionable, the chemist may calculate and report a maximum possible concentration (flagged as < the numerical value) which allows the data user to determine if additional sampling is required or, if the reported concentration is below action levels and project objectives and Data Quality Objectives (DQOs) have been met, to forego further analysis.

Similarly, when sample concentration exceeds the linear range, the analyst may report a probable minimum level (flagged as > the numerical value) which allows the data user to determine if additional sampling is required or, if the reported concentration is above action levels and project objectives and DQOs have been met, to forego further analysis.

QC criteria as described in FASP QC SOPs must be met for all analyses. Advisory limits for spike %R and duplicate RPD for VOCs in soil/sediment, water, and air/soil gas are presented in Tables 6, 7, and 8, respectively.

11.0 METHOD PERFORMANCE

Retention time and magnitude of peaks are used to identify VOCs present in the environmental sample. Examples of GC chromatograms for volatile organic FTCL analytes as detected by the PID and ECD methods are provided below.

TABLE 6

FASP MATRIX SPIKE PERCENT RECOVERY (%R) AND DUPLICATE RELATIVE PERCENT DIFFERENCE (RPD) ADVISORY LIMITS FOR VOCs IN SOIL/SEDIMENT

Analyte	FASP Advisory Quality Control Limits[a]	
	Spike %R (%)	Duplicate RPD (%)
Benzene	30 - 200	± 100
Bromodichloromethane	30 - 200	± 100
Bromomethane (Methyl Bromide)	30 - 200	± 100
Chlorobenzene	30 - 200	± 100
(2-Chloroethoxy)ethene (2-Chloroethyl Vinyl Ether)	30 - 200	± 100
Chloroethylene (Vinyl Chloride)	30 - 200	± 100
Carbon Tetrachloride	30 - 200	± 100
Dibromochloromethane	30 - 200	± 100
1,1-Dichloroethane (Ethylidene Chloride)	30 - 200	± 100
1,2-Dichloroethane (Ethylene Dichloride)	30 - 200	± 100
1,1-Dichloroethene (Vinylidene Chloride)	30 - 200	± 100
trans-1,2-Dichloroethene (Acetylene Dichloride)	30 - 200	± 100
Dichloromethane (Methylene Chloride)	30 - 200	± 100
1,2-Dichloropropane (Propylene Dichloride)	30 - 200	± 100
1,3-Dichloropropene (Dichloropropylene)	30 - 200	± 100
o,m,p-Dimethylbenzene (Xylenes)	30 - 200	± 100
Ethylbenzene	30 - 200	± 100
Methylbenzene (Toluene)	30 - 200	± 100
2-Propenal (Acrolein, Acrylaldehyde)	30 - 200	± 100
2-Propenenitrile (Acrylonitrile)	30 - 200	± 100
1,1,2,2-Tetrachloroethane	30 - 200	± 100
Tetrachloroethene (Tetrachloroethylene)	30 - 200	± 100
Tribromoethane (Bromoform)	30 - 200	± 100
1,1,1-Trichloroethane (Methyl Chloroform)	30 - 200	± 100
1,1,2-Trichloroethane (Vinyl Trichloride)	30 - 200	± 100
Trichloroethene (Trichloroethylene)	30 - 200	± 100
Trichlorofluoromethane	30 - 200	± 100
Trichloromethane (Chloroform)	30 - 200	± 100

[a] If the concentration of an FTCL analyte is less than five times the FQL, FASP advisory QC limits for duplicate RPD values become ±3 times the FQL for that individual analyte.

TABLE 7

FASP MATRIX SPIKE PERCENT RECOVERY (%R) AND DUPLICATE RELATIVE PERCENT DIFFERENCE (RPD) ADVISORY LIMITS FOR VOCs IN WATER

Analyte	FASP Advisory Quality Control Limits[a] Spike %R (%)	Duplicate RPD (%)
Benzene	30 - 150	± 75
Bromodichloromethane	30 - 150	± 75
Bromomethane (Methyl Bromide)	30 - 150	± 75
Chlorobenzene	30 - 150	± 75
(2-Chloroethoxy)ethene (2-Chloroethyl Vinyl Ether)	30 - 150	± 75
Chloroethylene (Vinyl Chloride)	30 - 150	± 75
Carbon Tetrachloride	30 - 150	± 75
Dibromochloromethane	30 - 150	± 75
1,1-Dichloroethane (Ethylidene Chloride)	30 - 150	± 75
1,2-Dichloroethane (Ethylene Dichloride)	30 - 150	± 75
1,1-Dichloroethene (Vinylidene Chloride)	30 - 150	± 75
trans-1,2-Dichloroethene (Acetylene Dichloride)	30 - 150	± 75
Dichloromethane (Methylene Chloride)	30 - 150	± 75
1,2-Dichloropropane (Propylene Dichloride)	30 - 150	± 75
1,3-Dichloropropene (Dichloropropylene)	30 - 150	± 75
o,m,p-Dimethylbenzene (Xylenes)	30 - 150	± 75
Ethylbenzene	30 - 150	± 75
Methylbenzene (Toluene)	30 - 150	± 75
2-Propenal (Acrolein, Acrylaldehyde)	30 - 150	± 75
2-Propenenitrile (Acrylonitrile)	30 - 150	± 75
1,1,2,2-Tetrachloroethane	30 - 150	± 75
Tetrachloroethene (Tetrachloroethylene)	30 - 150	± 75
Tribromoethane (Bromoform)	30 - 150	± 75
1,1,1-Trichloroethane (Methyl Chloroform)	30 - 150	± 75
1,1,2-Trichloroethane (Vinyl Trichloride)	30 - 150	± 75
Trichloroethene (Trichloroethylene)	30 - 150	± 75
Trichlorofluoromethane	30 - 150	± 75
Trichloromethane (Chloroform)	30 - 150	± 75

[a] If the concentration of an FTCL analyte is less than five times the FQL, FASP advisory QC limits for duplicate RPD values become ±3 times the FQL for that individual analyte.

TABLE 8

FASP MATRIX SPIKE PERCENT RECOVERY (%R) AND DUPLICATE RELATIVE PERCENT DIFFERENCE (RPD) ADVISORY LIMITS FOR VOCs IN SOIL GAS

Analyte	FASP Advisory Quality Control Limits[a]	
	Spike %R (%)	Duplicate RPD (%)
Benzene	30 - 150	± 75
Bromodichloromethane	30 - 150	± 75
Bromomethane (Methyl Bromide)	30 - 150	± 75
Chlorobenzene	30 - 150	± 75
(2-Chloroethoxy)ethene (2-Chloroethyl Vinyl Ether)	30 - 150	± 75
Chloroethylene (Vinyl Chloride)	30 - 150	± 75
Carbon Tetrachloride	30 - 150	± 75
Dibromochloromethane	30 - 150	± 75
1,1-Dichloroethane (Ethylidene Chloride)	30 - 150	± 75
1,2-Dichloroethane (Ethylene Dichloride)	30 - 150	± 75
1,1-Dichloroethene (Vinylidene Chloride)	30 - 150	± 75
trans-1,2-Dichloroethene (Acetylene Dichloride)	30 - 150	± 75
Dichloromethane (Methylene Chloride)	30 - 150	± 75
1,2-Dichloropropane (Propylene Dichloride)	30 - 150	± 75
1,3-Dichloropropene (Dichloropropylene)	30 - 150	± 75
o,m,p-Dimethylbenzene (Xylenes)	30 - 150	± 75
Ethylbenzene	30 - 150	± 75
Methylbenzene (Toluene)	30 - 150	± 75
2-Propenal (Acrolein, Acrylaldehyde)	30 - 150	± 75
2-Propenenitrile (Acrylonitrile)	30 - 150	± 75
1,1,2,2-Tetrachloroethane	30 - 150	± 75
Tetrachloroethene (Tetrachloroethylene)	30 - 150	± 75
Tribromoethane (Bromoform)	30 - 150	± 75
1,1,1-Trichloroethane (Methyl Chloroform)	30 - 150	± 75
1,1,2-Trichloroethane (Vinyl Trichloride)	30 - 150	± 75
Trichloroethene (Trichloroethylene)	30 - 150	± 75
Trichlorofluoromethane	30 - 150	± 75
Trichloromethane (Chloroform)	30 - 150	± 75

[a] If the concentration of an FTCL analyte is less than five times the FQL, FASP advisory QC limits for duplicate RPD values become ±3 times the FQL for that individual analyte.

11.1 GAS CHROMATOGRAM A - PID

CHROMATOGRAM WILL FOLLOW BY FRIDAY

Column: J&W 30 m x 0.53 mm I.D. DB-624 fused silica megabore capillary column.

Column Temperature: Initial temperature 35 °C for 4 mins. Ramp 4 ° C/min. Final temperature 105 °C.

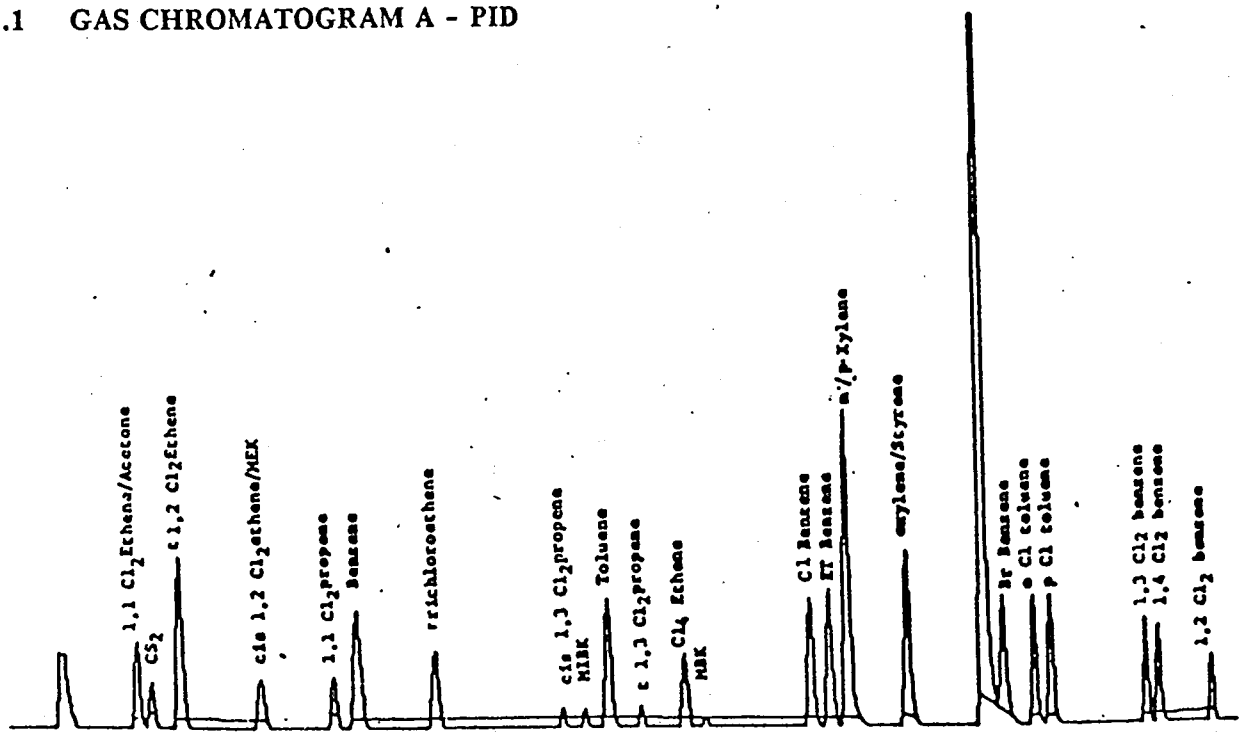
Detector/Injector Temperature: 150 °C

Gas: Carrier; zero grade nitrogen, 10 ml/min.
Auxiliary; zero grade nitrogen, 40 ml/min.

11.0 METHOD PERFORMANCE

The following are examples of GC chromatograms for volatile organic FTCL analytes as detected by the PID and electron capture detectors.

11.1 GAS CHROMATOGRAM A - PID



Column: J&W 30 m x 0.53 mm I.D. DB-624 fused silica megabore capillary column.

Column Temperature: Initial temperature 35°C for 4 mins. Ramp 4° C/min. Final temperature 105°C.

Detector/Injector Temperature: 150°C

Gas: Carrier; ultrapure nitrogen, 10 ml/min.
Make-up; ultrapure nitrogen, 40 ml/min.

Detector: HNu PID with a 10.2 eV lamp.

Detector: HNu PID with a 10.2 eV lamp.

11.2 GAS CHROMATOGRAM B - ECD

CHROMATOGRAM WILL FOLLOW BY FRIDAY

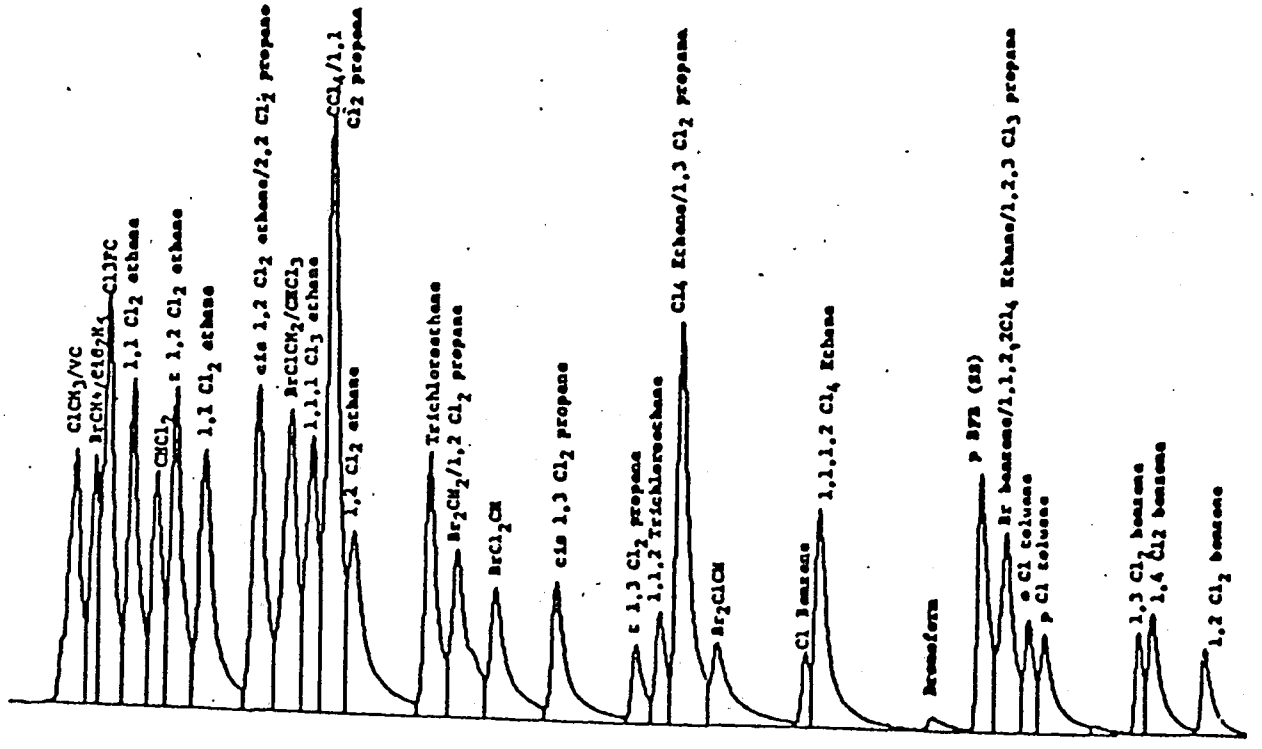
Column: J&W 30m x 0.53 mm I.D. DB-624 fused silica megabore capillary column.

Column Temperature: Initial temperature 35 °C for 4 mins. Ramp 4 °C/min.
Final temperature 105 °C.

Detector Injector Temperature: 150 °C

Gas: Carrier; zero grade nitrogen, 10 ml/min.
Auxiliary; zero grade nitrogen, 40 ml/min.

11.2 GAS CHROMATOGRAM B - ECD



Column: J&W 30m x 0.53 mm I.D. DB-624 fused silica megabore capillary column.

Column Temperature: Initial temperature 35°C for 4 mins. Ramp 4°C/min.
Final temperature 105°C.

Detector Injector Temperature: 150°C

Gas: Carrier; ultrapure nitrogen, 10 ml/min.
Make-up; ultrapure nitrogen, 40 ml/min.

Detector: Electron Capture Detector (ECD)

Detector: Electron Capture Detector (ECD)

12.0 DELIVERABLE DOCUMENTATION

The on-site laboratory will provide the sampling team with current analytical result information. Optional efficiency is achieved when preliminary analytical summaries can be produced within 24 hours of sample collection. A preliminary summary will be followed by a final FASP report documenting specific details of the entire analytical procedure.

12.1 PRELIMINARY SUMMARY OF SAMPLE RESULTS

A preliminary summary of sample results should be available within 24 hours of sample analysis by the laboratory. Analytical data will be tabulated and provided to the sampling team so that decisions can be made in the field. These summaries will include sample numbers, time, date, and location of collection, and concentrations of analytes.

12.2 FINAL FASP REPORT

The final FASP report generated for the project will include the following:

1) A reference to the FASP method used and notes addressing any changes to method.

2) A hard copy of all data and summary sheets documenting required QA/QC data (available within 14 days of completion of all FASP analyses for the project).

3) A data summary of all reportable results with units (μg/kg or μg/l) clearly specified.

4) All calculations, which will be performed using standard good measurement practices.

5) A statement by analyst that initial, continuing, and final CFs, %RSDs, and RPDs FASP QC were met.

6) A summary table of the blank, matrix spike, and duplicate results for each target analyte.

7) A summary of FQLs for each target analyte is also a final deliverable requirement.

8) A comparison of interlaboratory sample results will be submitted as an addendum to the final FASP report.

All results will be annotated (followed by the flag, F) by the laboratory to indicate to future data users that FASP techniques were used in sample analysis.

13.0 SAMPLE AND DATA STORAGE

This section discusses the disposal of analyte samples, reagents, and other generated laboratory wastes. It also discusses raw, summary, and permanent data storage.

13.1 DISPOSAL OF SAMPLES

Samples and laboratory waste will be disposed of in accordance with specific project procedures for solid and liquid waste established in the Quality Assurance Project Plan (QAPjP).

13.2 RAW AND SUMMARY DATA STORAGE

The laboratory will maintain a hard copy or computer disk storage of all raw (including calculations, instrument printouts, log books, and bench sheets) and summary data associated with an analytical project for a minimum of 6 months after receipt of the hard copy report by the data user.

13.3 PERMANENT DATA STORAGE

After the 6-month period has elapsed, the laboratory will place all records, including laboratory notebooks, into permanent storage files.

APPENDIX B
STANDARD OPERATING GUIDELINES FOR THE ANALYSIS OF PAHS IN SOILS

DRAFT

FASP STANDARD OPERATING GUIDELINE

Polycyclic Aromatic Hydrocarbons (PAHs) In Soil

Method F060.001

DISCLAIMER

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1.0 SCOPE, APPLICATION, AND LIMITATIONS

1.1 PURPOSE

This Field Analytical Support Project (FASP) method is proposed for use in determining the concentrations of various polycyclic aromatic hydrocarbons (PAHs) in soil/sediment samples.

1.2 LIST OF COMPOUNDS

Table 1-1 lists the compounds that may be determined by this method and approximate method quantitation limits.

1.3 USER RESTRICTIONS

The method should be used only by trained analysts under the supervision of an experienced Chemist.

1.4 ANALYTES IDENTIFIED

The method yields tentative identification and estimated quantitation of the analytes listed in Table 1-1. Report values are on as-received basis--no dry weights are used.

1.5 VERIFICATION

The primary objective of FASP is to provide analytical data in a timely manner for guidance of ongoing work in the field. Identification of specific target compounds and prior knowledge regarding potential matrix interferences are prerequisites to successful use of FASP. FASP is not equivalent to or a replacement for Contract Laboratory Program (CLP) Analyses. Verification of data through the CLP, encompassing the range of sample concentrations, is recommended.

1.6 QUALITY CONTROL

This FASP SOG should be used in conjunction with FASP SOGs for quality control (QC)--General Quality Control (F030.001), Quality Control-Gas Chromatographic Compound Analyses (F030.002) and Laboratory Safety (F020.001).

Table 1-1

FASP TARGET COMPOUND LIST (FTCL) AND
FASP QUANTITATION LIMITS (FQL)[a]

PAH	CAS NUMBER	Quantitation Limits[b] in Soil/Sediment (µg/kg)
Naphthalene	91-20-3	1,000
Acenaphthylene	208-96-8	1,000
Acenaphthene	83-32-0	1,000
Fluorene	86-73-7	1,000
Phenanthrene	85-01-8	1,000
Anthracene	120-12-7	1,000
Fluoranthene	206-44-0	1,000
Pyrene	129-00-0	1,000
Chrysene	218-01-9	1,000
Benzo(a)anthracene	56-55-3	1,000
Benzo(b)fluoranthene[b]	205-00-2	1,000
Benzo(k)fluoranthene[b]	207-08-9	1,000
Benzo(a)pyrene	52-32-8	1,000
Indeno(1,2,3-cd)pyrene[c]	193-39-5	1,000
Dibenzo(a,h)anthracene[c]	53-70-3	1,000
Benzo(g,h,i)perylene	191-24-2	1,000

[a] Specific quantitation limit values are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

[b] Quantitation limits listed for soil/sediment are on an as-received basis.

[c] These compounds coelute.

[d] These compounds coelute.

2.0 SUMMARY OF METHOD

A measured amount of soil is placed in a screw-cap culture tube. The sample is extracted twice with a measured volume of methylene chloride. Isolation of target analytes is accomplished by silica gel cleanup of the extract to eliminate interferences (primarily aliphatic hydrocarbons). Analysis is performed using a temperature programmed gas chromatograph (GC) with a megabore capillary column or a packed column, and a flame ionization detector (FID). Identification is based on comparison of retention times between samples and standards. Quantitation is by the external standard method.

3.0 INTERFERENCES

Interferences may be minimized by use of pesticide grade or ultrapure reagents, exhaustive cleanup of glassware, and avoidance of plastic materials in laboratory operations. The analytical system must be demonstrated to be free from contamination under conditions of the analysis by running laboratory reagent blanks.

GC interference by sample carryover may be minimized by use of disposable glassware during sample preparation and employing the maximum possible rinse cycle on automatic injection systems or by thoroughly rinsing syringes employed in manual injections.

Interferences coextracted from samples are matrix and site specific. It is possible that cleanups used in either FASP or Regular Analytical Services (RAS) CLP methods may fail to eliminate interferences. Highly specialized CLP Special Analytical Services (SAS) techniques may be required to produce acceptable analytical results.

4.0 APPARATUS AND MATERIALS

4.1 ANALYTICAL SYSTEMS

Listed below are two GC options that meet the requirements of this method. Other GC configurations may be substituted if they meet the method requirements.

1) Gas Chromatograph, Option 1

An analytical system complete with a temperature-programmable GC and all necessary accessories including detector and injector systems designed or modified to accept megabore capillary analytical columns is required. The system shall have a data handling system attached to the detector that is capable of retention time labeling, relative retention time comparisons, and providing peak height and peak area measurements.

1) Column 1 - 1.8 m x 3.0 mm I.D. glass column packed with 3% SP-2250 on 100/120 Supelcoport (Supelco), or equivalent.

2) Column 2 - 1.8 m x 3.0 mm I.D. glass column packed with 3% OV-1 on 100/120 Supelcoport (Supelco), or equivalent.

3) Detector - Flame Ionization Detector (FID) with optional makeup gas supply at the detector's inlet.

4) Gas Supply - The carrier gas and makeup gas (if required) should be ultrapure helium or nitrogen. The flame gases are zero air and ultrapure hydrogen or equivalent. All gases should pass through hydrocarbon traps prior to the GC.

2) Gas Chromatograph, Option 2

An analytical system complete with a temperature programmable GC and all necessary accessories including injector and detector systems designed or modified to accept megabore capillary analytical columns is required. The system shall have a data handling system attached to the detector that is capable of retention time labeling, relative retention time comparisons, and providing peak height and peak area measurements.

1) Column - 15 m x 0.53 mm I.D. DB-5 fused silica capillary column (FSCC) (J&W Scientific), or equivalent.

2) Detector - FID using a system with makeup gas supply at the detector's capillary inlet.

3) Gas Supply - The carrier gas and makeup should be ultrapure helium or nitrogen. The flame gases are zero air and ultrapure hydrogen or equivalent. All gases should pass through hydrocarbon traps prior to the GC.

4.2 OTHER LABORATORY EQUIPMENT

1) Glass Wool

Heat at 200°C for 24 hours and store in glass jars with Teflon-lined caps.

2) Screw Cap Culture Tubes

Disposable 16 mm x 150 mm borosilicate glass culture tubes with Teflon-lined phenolic caps for extraction.

3) Disposable Pipets

Pasteur, 6 and 9 inches long.
Giant, 10 mm O.D. x 6 inches long.

4) Spatulas

Stainless steel, micro and semimicro.

5) Microsyringe

10 µL.

6) Balance

Top loading, capable of weighing to 0.01 g, used to weight samples.

7) Micropipets

10-1,000 µL.

8) Volumetric Pipets/Repipets

0.5, 1.0, 5, 10, and 25 mL.

9) Volumetric Flasks

10, 25, 50, 100 mL.

10) Vortex Mixer

Vortex Genie or equivalent.

11) Centrifuge

Capable of holding 16 mm x 150 mm culture tubes.

12) Amber Storage Bottles

100 and 500 mL.

13) Autosampler Vials

1 or 2 mL with Teflon-lined screw caps.

14) Graduated Centrifuge Tubes

15 mL with ground glass stoppers.

15) Hydrocarbon Traps

Supelpure-HC-Trap or equivalent.

16) Leak Detector

Snoop Liquid, or equivalent, for packed-column operations, and GOW-MAC Gas Leak Detector, or equivalent, for megabore capillary operations.

17) Timer

0 to 10 minute range.

18) Teflon Wash Bottles

500 mL.

19) Chromatographic Data Stamp

Used to record instrument operating conditions.

20) Nitrogen Evaporation System

N-Evap, or equivalent.

21) Laboratory Oven

Capable of maintaining temperatures of greater than or equal to 200°C.

4.3 REGION-SPECIFIC INSTRUMENT OPTIONS

Region-specific instrument options are provided in Appendix A of this method.

5.0 REAGENTS

5.1 SOLVENTS

1) Petroleum ether, pesticide quality, or equivalent.

2) Methylene chloride, pesticide quality, or equivalent.

3) Isooctane, pesticide quality, or equivalent.

5.2 MISCELLANEOUS REAGENTS

1) Reagent Water

Reagent water is defined as water in which an interferent is not observed at the FASP Quantitation Limit (FQL) of the analyte of interest. Reagent water may be generated using a carbon filter bed containing activated carbon (Calgon Corporation, Filtrasorb-300 or equivalent) or a water purification system (Milli-Q Plus with Organex Q cartridge or equivalent).

2) Sodium Sulfate

Reagent, anhydrous, granular. The sodium sulfate is reconditioned by heating for 24 hours at 200°C and storing in clean glass containers with Teflon-lined covers.

3) Silica Gel

Grade 923, mesh 100/200. Activate the gel for 16 hours at 130°C in a shallow glass tray loosely covered with foil. The gel may be stored for up to 1 week in glass jars with Teflon-lined covers.

5.3 GASES

1) Helium

Ultrapure or chromatographic grade (always used in conjunction with a hydrocarbon trap).

2) Nitrogen

Ultrapure or chromatographic grade (always used in conjunction with a hydrocarbon trap).

3) Zero Air

Zero grade or chromatographic grade (always used in conjunction with a hydrocarbon trap).

4) Hydrogen

Ultrapure or chromatographic grade (always used in conjunction with a hydrocarbon trap).

5.4 STOCK STANDARD SOLUTIONS

Stock standard solutions or analytes should be purchased as manufacturer certified solutions. Single PAH standards may be used; however, standard mixtures of PAHs are recommended.

5.5 CALIBRATION STANDARDS

Prepare calibration standards at a minimum of three concentration levels for each analyte of interest. This is done through volumetric dilution of the stock standards with isooctane. The lowest concentration standard should be approximately two times the FQL as listed in Table 1-1. The remaining standard concentrations should define the approximate working range of the GC: one at the upper linear range and the other midway between it and the lowest standard. All standards must be stored at 4°C in Teflon-sealed glass bottles. Calibration solutions must be replaced after 6 months, or whenever comparison with check standards indicates a problem.

5.6 CHECK STANDARDS

Check standards are calibration standards independently prepared by a chemist other than the calibration standard preparer.

5.7 MATRIX SPIKE SOLUTIONS

Matrix spike solutions should be prepared by dilution of stock standard solutions so that no more than 250 μL of spike solution is required to provide a final sample spike level within FASP QC limits.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples should be collected, handled, preserved, and shipped maintaining a chain-of-custody following current EPA regulations and recommendations in force at the time of sample collection. The sole exceptions to this rule are the sample volumes required by the laboratory. Soil samples should be shipped in 4-oz wide-mouthed glass jars with Teflon-lined caps.

The use of chain-of-custody records as described in the U.S. EPA "CLP Users Guide" (9240.0-1), December 1988, is required for sample tracking. The maximum holding times for soil PAH samples are 7 days between collection and extraction, and 40 days between extraction and analysis.

7.0 CALIBRATION

7.1 INITIAL CALIBRATION

After an experienced chromatographer has ensured that the entire chromatographic system is functioning properly; i.e., conditions exist such that resolution, retention times, response reporting, and interpretation of chromatographic spectra are within acceptable quality control limits, the GC may be calibrated (Section 11). Using at least three calibration standards for each PAH target analyte prepared as described in Section 5.10, initial calibration curves (response versus mass of standard injected) are generated for each PAH target analyte (refer to Section 10 for chromatographic procedures).

The percent relative standard deviation (%RSD, see Section 11) based on each PAH target analyte's three Calibration Factors (CFs, see Section 11) is computed to determine the acceptability (linearity) of the curve. Unless otherwise specified the %RSD must be $\leq$ 25 percent or the calibration is invalid and must be repeated. Any time the GC system is altered (e.g., new column, or change in gas supply, change in oven temperature) or shut down, a new initial calibration curve must be established.

7.2 CONTINUING CALIBRATION

The GC system is rechecked on a regular basis through the continuing calibration. The midrange initial calibration standard is generally the most appropriate choice for continuing calibration validation. This single point analysis follows the same analytical procedures used in the initial calibration. Instrument response is used to compute the CF, which is then compared to the mean initial calibration factor (CF), and a relative percent difference (RPD, see Section11) is calculated. Unless otherwise specified, the RPD must be $\leq$ 25 percent for the continuing calibration to be considered valid. Otherwise, the calibration must be repeated. A continuing calibration remains valid for a maximum of 24 hours providing the GC system remains unaltered during that time.

The continuing calibration is used in all target analyte sample concentration calculations (Section 11) for the period over which the calibration has been validated.

7.3 FINAL CALIBRATION

The final calibration must be obtained at the end of each batch of sample analyses. The maximum allowable RPD between the mean initial calibration and the final calibration factors for each analyte must be $\leq$ 50 percent. A final calibration that achieves $\leq$ 25 percent RPD may be used as an ongoing continuing calibration.

8.0 EXTRACTION

The sample extraction technique for PAHs in soil or sediment is as follows:

1) Add 2 to 3 grams of well-homogenized sample to a tared and labeled 150 mm culture tube; reweigh to the nearest 0.01 g. Record weights.

2) Add 6 mL of methylene chloride by repipet to the culture tube and cap.

3) Vortex at maximum speed for 2 minutes.

4) Centrifuge sample for 5 minutes.

5) Quantitatively decant the solvent using a disposable pasteur pipet into a clean 150-mm culture tube.

6) Repeat steps 2 through 5, combining the extracts.

7) Add a small quantity of anhydrous sodium sulfate to the extract and vortex for 30 seconds.

8) Add 2 mL of isooctane and vortex for 10 seconds.

9) Reduce the solvent volume to approximately 1.0 mL with gentle heat under a N_2 stream.

10) Extract ready for cleanup.

9.0 CLEANUP

The use of a silica gel chromatography column as part of a routine cleanup procedure may not be necessary in all cases, but is required for all samples as a general precaution. Clean extracts extend both column and detector life, and provide more accurate and precise data. Technique gained through experience is critical in column chromatography. Columns must not be allowed to lose their slurry characteristics, or channeling may significantly reduce cleanup effectiveness. Mixing between solvents must be minimized to avoid poor chromatographic separations.

9.1 SILICA GEL COLUMN PREPARATION

1) Place a small slug of muffle-furnaced glass wool into a 10 mm O.D. (4 mL) giant pipet.

2) Add 1.8 g of activated silica gel to the column.

3) Add a 1 cm layer of anhydrous sodium sulfate on top of the silica gel.

4) Rinse the column with 10 mL of methylene chloride and discard the rinsate. From this point on, the column must <u>not</u> be allowed to go dry until the cleanup is completed.

5) Rinse the column with 10 mL of petroleum ether and discard the rinsate.

9.2 GENERAL EXTRACT CLEANUP

1) Add the concentrated sample extract (Section 8) to the column using a small disposable pipet.

2) Rinse the extract culture tube with two 0.5 mL aliquots of isooctane and add the rinsate to the column.

3) Elute the column with 6.0 mL of petroleum ether and discard the solvent.

4) Elute the column with 10 mL of methylene chloride. Collect the first 10 mL of eluted solvent in a graduated centrifuge tube.

5) For highly contaminated samples, the extract is now ready for GC injection. However, in most cases, greater sensitivity is required and is achieved by proceeding as follows:

6) Reduce the solvent volume to less than 1 mL with low heat under a nitrogen stream.

7) Stopper the centrifuge tube and allow to cool. Record the volume.

8) The sample extract is now ready for GC injection.

9.3 SOLID PHASE EXTRACTION TECHNOLOGY

Solid phase extraction (SPE) technology (e.g., Sep-Pak) may provide an acceptable alternative to acid cleanup for PAH extracts if method validation studies are conducted to provide evidence of their utility. However, in-house testing has shown blank contamination from SPE materials prohibits their use.

9.4 CLP RAS/SAS ANALYSES

FAST methodologies, including cleanup, may not be sufficient to continue acceptable analyses. In such cases, CLP RAS/SAS analyses be the only acceptable alternatives.

10.0 INSTRUMENTAL ANALYSIS

10.1 INSTRUMENT PARAMETERS

Table 10-1 summarizes an example of acceptable instrument operating conditions for the GC. Other instruments, columns, and chromatographic conditions may be used if FAST QC criteria are met.

Table 10-1

EXAMPLE FASP GC OPERATING CONDITIONS

Instrument:	Shimadzu GC Mini-2 equipped with FID modified to accept megabore capillary columns and a Shimadzu TP-M2R temperature programmer.
Integrator:	Shimadzu Chromatopac C-R3A Data Processor.
Column:	J&W 15 m x 0.53 mm DB-5 fused silica megabore capillary column.
Carrier Gas:	Ultrapure Helium or Nitrogen, at a flowrate of 10 mL/min.
Detector Gas:	Zero air at a flowrate of 300 mL/min; ultrapure hydrogen at a flowrate of 40 mL/min.
Column (oven) Temperature Program:	Initial temperature: 75°C for 2 mins. Ramp at 15°C/min. Final temperature: 310°C for 7 mins.
Injector Temperature:	330°C.
Detector Temperature:	330°C.
GC Analysis Time:	Approximately 25 mins.
Standard/ Sample Injection:	Solvent flush manual injection or automated sample injection is recommended for PAH analysis. Two microliters of nanograde methylene chloride, 0.5 µL of air, and 2.0 and 3.0 µL (measured to the nearest 0.05 µL) of sample extract are sequentially drawn into a 10-µL syringe and immediately injected into the GC.

10.2 CHROMATOGRAMS

Computer reproduction of chromatograms that are attenuated to ensure all peaks are on scale over a 100-fold range are acceptable. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Generally, peak response should be > 25 percent and < 100 percent of full-scale deflection to allow visual recognition of the various PAH compounds.

The following information must be recorded on each chromatogram.

1) Instrument and detector identification;
2) Column packing, coating, length, and I.D.;
3) Oven temperature;
4) Injector/detector temperature;
5) Gas and flow;
6) Site name;
7) Sample number;
8) Date and time; and
9) GC operator initials.

10.3 PAH IDENTIFICATION

Qualitative identification of PAHs is based on retention time as compared to standards on a single column. A second, dissimilar column may be used to assist in identification.

Generally, individual peak retention time windows should be ≤ 2 percent for megabore capillary columns (≤ 5 percent for packed columns).

It may not be possible or practical to separate all target analyte PAHs on a single column. In such cases these target analytes should be denoted as the appropriate combination of PAHs.

It is possible that interferences may preclude positive identification of an analyte. In such cases, the chemists should report the presence of the interferents with the maximum possible PAH concentration (see Section 9 and 11.4).

10.4 REGION-SPECIFIC INSTRUMENT PARAMETERS

Specific instrument operating parameters are provided in Appendix B of this method.

10.5 ANALYTICAL SEQUENCE

1) Instrument blank.

2) Initial calibration

3) Check standard solution and/or performance evaluation sample (if available).

4) Continuing calibration; repeat within 24 hours of previous continuing calibration.

5) Associated QC lot method blank.

6) Twenty samples and associated QC lot spike and duplicate.

7) Repeat sequence beginning at Step 5 until all sample analyses are completed or another continuing calibration is required.

8) Final calibration when all sample analyses are complete.

11.0 CALCULATIONS

11.1 INITIAL CALIBRATION

GC response to PAH target analytes is measured by determining Calibration Factors (CFs). In the case of coeluted analytes, the summed areas and masses should be employed to generate a combined CF for the target analyte PAHs. Calculate the CF for each PAH target analyte in the initial standard. The integrator may be used to make all of these computations.

$$CF = \frac{\text{Area of Peak}}{\text{Mass Injected (in nanograms)}}$$

Using the calibration factors, calculate the percent relative standard deviation (%RSD) for each PAH target analyte at a minimum of three concentration levels using the following equation.

$$\%\ RSD = \frac{SD}{X} \times 100$$

where SD. the Standard Deviation, is given by

where: X_i = individual calibration factor (per analyte),
$\bar{X}$ = mean of initial three calibration factors (per analyte),
N = number of calibration standards.

The %RSD must be ≤ 25.0 percent.

11.2 CONTINUING CALIBRATION

Sample quantitation is based on analyte calibration factors calculated from continuing calibrations. Midrange standards for all initial calibration PAH target analytes must be analyzed at specified intervals (≤ 24 hours).

The maximum allowable relative percent difference (RPD) calculated using the equation below for each analyte must be ≤ 25 percent.

where: CF_I = mean CF from the initial calibration for each analyte
CF_C = measured CF from the continuing calibration for the same analyte

11.3 FINAL CALIBRATION

The final calibration is obtained at the end of any batch of samples analyzed.

The maximum allowable RPD between the mean initial calibration and final calibration factors for each PAH target analyte must be ≤ 50 percent. A final calibration that achieves ≤ 25 percent RPD may be used as an ongoing continuing calibration.

where: CF_I = mean CF from the initial calibration for each analyte
CF_F = final CF for the same analyte

11.4 SAMPLE QUANTITATION

Calculate the concentration in the sample using the following equation for external standards. The response can be measured by automated peak height or peak area measurements from an integrator. Sample quantitation is based on analyte calibration factors calculated from continuing calibrations.

$$\text{Concentration } (\mu g/kg) \text{ (Wet weight)} = \frac{(A_x)(V_t)(D)}{(CF_c)(V_i)(V_s)}$$

where: A_x = response for the analyte to be measured

CF_c = CF from the continuing calibration for the same analyte

V_i = volume of extract injected (μL)

V_t = volume of total extract (μL)

W_s = weight of sample extracted (g)

D = dilution factor if used

Report results in micrograms per kilogram (μg/kg) without correction for blank, spike recovery, or percent moisture.

Coeluted analytes should be quantitated and reported as the combination of the unseparated PAH target analytes.

Sample spectra may not match identically with those of analytical standards. When positive identification is questionable, the chemist may calculate and report a maximum possible concentration (flagged as < the numerical value) that allows the data user to determine if additional (e.g., CLP RAS or SAS) work is required or--if the reported concentration is below action levels and project objectives and DQOs have been met, to forego further analysis.

Similarly, when sample concentration exceeds the linear range, the analyst may report a probable minimum level (flagged as > the numerical value) which allows the data user to determine if additional (e.g., CLP RAS or SAS) work is required, or--if the reported concentration is above action levels and project objectives and DQOs have been met--to forego further analysis.

QC criteria (as described in FASP QC SOGs) must be met for all analyses. Advisory limits for spike %R and duplicate RPD are presented in Table 11-1.

Table 11-1

FASP MATRIX SPIKE PERCENT RECOVERY (%R) AND DUPLICATE RELATIVE PERCENT DIFFERENCE (RPD) ADVISORY LIMITS METHOD F060.001 (PAHs IN SOIL)

Analyte	FASP Advisory Quality Control Limits[a]	
	Spike %R (%)	Duplicate RPD (%)
Naphthalene	30 - 200	± 100
Acenaphthylene	30 - 200	± 100
Acenaphthene	30 - 200	± 100
Fluorene	30 - 200	± 100
Phenanthrene	30 - 200	± 100
Anthracene	30 - 200	± 100
Fluoranthene	30 - 200	± 100
Pyrene	30 - 200	± 100
Benzo(a)anthracene	30 - 200	± 100
Chrysene	30 - 200	± 100
Benzo(b)fluoranthene[b]		
Benzo(k)fluoranthene[b]	30 - 200	± 100
Benzo(a)pyrene	30 - 200	± 100
Indeno(1,2,3-cd)pyrene[c]		
Dibenzo(a,h)anthracene[c]	30 - 200	± 100
Benzo(g,h,i)perylene	30 - 200	± 100

[a] If the concentration of an FTCL analyte is less than five times the FQL, FASP advisory control limits for duplicate RPD values become ±3 times the FQL for that individual analyte.

[b] Coeluting analytes.

[c] Coeluting analytes.

12.0 METHOD PERFORMANCE

The following chromatogram is an example of a GC spectra for several commonly encountered PAHs.

12.1 GAS CHROMATOGRAM - PAH COMPOUNDS

Column: 15 m x 0.53 mm DB-5 fused silica megabore capillary

Column Temperature Program: Initial 75°C - 2 mins; ramp 15°C per minute; final 310°C - 7 mins

Detector/Injector Temperature: 330°C

Carrier Gas: Helium at 10 mL/min

Detector: FID

12.2 FASP METHOD F060.001 EXAMPLES OF QA/QC RESULTS

Spike triplicate, and split sample results are presented as examples of FASP Method F060.001 empirical data in Tables 12-1, 12-2, and 12-3, respectively.

Table 12-1

FAST METHOD F060.001
SOIL MATRIX SPIKE PERCENT RECOVERY (%R)

Analyte	Number of Samples	Mean %R %	Standard Deviation of %R %
Naphthalene	5	65	20
Acenaphthylene	9	76	19
Acenaphthene	5	51	7
Fluorene	5	87	14
Phenanthrene	9	65	19
Anthracene	5	88	12
Fluoranthene	9	70	15
Pyrene	5	87	12
Benzo(a)anthracene	5	77	13
Chrysene	5	80	21
Benzo(b)fluoranthene/ Benzo(k)fluoranthene	5	93	16
Benzo(a)pyrene	9	90	16
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	5	80	12
Benzo(g,h,i)perylene	9	91	22

Table 12-2

FASP METHOD F060.001
SOIL TRIPLICATE SAMPLE PRECISION

Analyte	Number of Triplicate Sample Groups	Mean %RSD %
Naphthalene	3	ND
Acenaphthylene	3	ND
Acenaphthene	3	ND
Fluorene	3	ND
Phenanthrene	3	49
Anthracene	3	45
Fluoranthene	3	40
Pyrene	3	44
Benzo(a)anthracene	3	46
Chrysene	3	46
Benzo(b)fluoranthene/ Benzo(k)fluoranthene	3	42
Benzo(a)pyrene	3	47
Indeno(1,2,3-cd)pyrene/ Dibenz(a,h)anthracene	3	10
Benzo(g,h,i)perylene	3	30

ND - Not detected in any sample.

Table 12-3

FASP METHOD F060.001
STATISTICAL COMPARISON OF FASP/CLP
METHOD SPLIT SAMPLE ANALYSES

Analyte	Number of Samples	Linear Regression Coefficient
Phenanthrene	6	-0.23
Anthracene	6	0.997
Fluoranthene	6	0.994
Pyrene	6	0.991
Chrysene/Benzo(a)anthracene	6	0.995
Benzo(b)fluoranthene/ Benzo(k)Fluoranthene	6	0.923
Benzo(a)pyrene	6	0.977
Indeno(1,2,3-cd)pyrene/ Dibenz(a,h)anthracene	3	0.48
Benzo(g,h,i)perylene	6	0.997

13.0 DELIVERIES

13.1 VERBAL SUMMARIES OF SAMPLE RESULTS

A verbal summary of sample results should be available within 24 hours of sample analysis by the laboratory or a facsimile type hard copy via telecommunication may be substituted. If computer compatibility can be established, a modem link may be used to transfer data from the laboratory to field personnel.

13.2 FINAL FASP REPORT

The final FASP report generated for each project should include the following considerations:

1) A reference to the FASP method used and a note addressing any changes to method.

2) A hard copy of all data and summary sheets documenting required QA/QC data (available within 14 days of completion of all FASP analyses for a project).

3) A data summary of all reportable results with units µg/kg clearly specified.

4) All calculations using standard good measurement practices in determining significant figures. Rounding off will be allowed only for final deliverable values.

5) All sample results reported using two significant figures. QC data will be reported in three significant figures.

6) A statement by analyte that initial, continuing, and final calibration CFs, %RSDs, and RPDs met FAST QC criteria.

7) A summary table of the blank, matrix spike, and duplicate results for each target analyte.

8) A summary of FQLs for each target analyte is also a final deliverable requirement.

9) A comparison of interlaboratory split sample results should be submitted as an addendum to the final FASP report.

Again, all results must be annotated (followed by the flag, F) by the laboratory to indicate to future data users that FASP techniques were used in sample analysis.

13.3 EXAMPLE FINAL REPORT

An example of a standard reporting format is provided in Appendix C of this method.

14.0 SAMPLE AND DATA STORAGE

14.1 DISPOSAL OF SAMPLES

Samples should be disposed of in accordance with established Federal, State, and local regulations and policies after a minimum holding period of 14 days after receipt by the laboratory. Sample extracts may be disposed of 30 days after final FASP report submission.

14.2 RAW AND SUMMARY DATA STORAGE

The lab must maintain a hard copy or computer disk storage of all raw (including instrument printouts and logbooks) and summary data associated with an analytical case for a minimum of 6 months after receipt of the hard copy report by the data user.

14.3 PERMANENT DATA STORAGE

After the 6-month period has elapsed, the laboratory should place all records, including laboratory notebooks, into permanent storage files.

APPENDIX A

FASP METHOD F060.001

E & E Region X FIT Instrument Options

GC System - Shimadzu GC-mini 2 with FID modified with a Direct Conversion and Makeup Gas Adapter for megabore capillary column operations.

Temperature Programmer - Shimadzu TP-M2R for temperature-programmed megabore capillary column analyses.

Date Handling System 1 - Shimadzu Data Processor Chromatopac C-RIB.

Data Handling System 2 - Shimadzu Data Processor Chromatopac C-R3A.

Data Handling System 3 - Shimadzu Data Processor Chromatopac C-R3A equipped with a CRT display unit and Shimadzu FDD-1A Floppy Disk Drive.

Data Handling System 4 - P.E. Nelson 2100 SW Integrator with 960 Series Intelligent Interface, Hyundai 80286 computer, and Epson LX800 printer.

APPENDIX B

FASP METHOD F060.001

E & E Region X FIT Instrument Parameters

Instrument: Shimadzu GC Mini-2 equipped with FID modified to accept megabore capillary columns and Shimadzu TP-M2R temperature programmer.

Integrator: Shimadzu Chromatopac C-R3A Data Processor.

Columns: J&W 15 m x 0.53 mm DB-5 fused silica megabore capillary column or Supelco 30 m x 0.75 mm SPB-5 borosilicate megabore capillary column.

Carrier Gas: Ultrapure helium or nitrogen, 10 mL/min.

Detector Gas: Zero air, 300 mL/min; ultrapure hydrogen, 40°C mL/min.

Column (Oven) Temperature: Initial temperature 75°C for 2 min. Ramp 15°C/min. Final temperature 310°C for 7 min.

Injector Temperature: 330°C.

Detector Temperature: 330°C.

APPENDIX C

FASP METHOD F060.001

EXAMPLE FINAL REPORT

October 1991

MEMORANDUM

DATE: May 18, 1999

TO: John White, FIT-RPO, US EPA Region X

THRU: Jeffrey Yellow, FIT-OM, E & E, Seattle

FROM: Tracy Red, Senior Chemist, E & E, Seattle

SUBJ: FASP Polycyclic Aromatic Hydrocarbon (PAH) Analytical Results
Smith Salvage
Jones, Oregon

REF: TDD F10-8903-100
PAN FOR0999SC

CC: Andrew Orange, FIT-RFC, E & E, Seattle
Gerald Black, DPO, US EPA, Region XX
Bruce Blue, ESD, US EPA, Region XX
Hunt Green, FASP-PM, E & E, Arlington

Transmitted herewithin are the results for the PAH analyses 10 samples from the Smith Salvage Site, Jones, Oregon.

TY:csr

Enclosures

October 1991

FASP POLYCYCLIC AROMATIC HYDROCARBON ANALYTICAL RESULTS

SMITH SALVAGE
JONES, OREGON

TDD F10-8903-100
PAN FORO999SC

Investigation Date: April 1999

FIT Analytical Team: Tracy Red and David Tan

Report Date: May 1999

Submitted to: John E. White, Regional Project Officer
Field Operations and Technical Support Branch
U.S. Environmental Protection Agency
Region XX
Seattle, Washington

October 1991

DISCLAIMER

This report has been prepared by Ecology and Environment, Inc. (E & E), under EPA Contract 68-01-7347. It has been reviewed and approved for public release by the U.S. Environmental Protection Agency (EPA). Mention of commercial products does not constitute endorsement by the U.S. Government. Technical content of this report is the responsibility of E & E, Seattle, Washington, and does not necessarily reflect the views or policies of the EPA.

1.0 INTRODUCTION

Analysis of 10 soil samples, collected at the Smith Salvage Site, was performed by Ecology and Environment, Inc. (E & E) Field Investigation Team (FIT) Chemists under Technical Directive Document (TDD) F10-8903-100, utilizing the E & E base laboratory in Seattle, Washington. The samples were analyzed for polycyclic aromatic hydrocarbons (PAHs) to acquire analytical data as an integral part of a Screening Site Inspection (SSI). In additional, three quality control samples were analyzed to monitor analytical method performance and to ensure data validity.

Samples were analyzed using the Standard Operating Guidelines for the Field Analytical Support Project FASP Method F060.001. As required by the USEPA, FASP data are annotated with the data qualifier "F" indicating that FASP methodologies were used to generate the data. As such, qualitative data are defined as tentatively identified and quantitative data should be interpreted as estimated quantities.

Samples were analyzed for the following PAHs:

Naphthalene	Chrysene
Acenaphthylene	Benzo(a)anthracene
Acenaphthene	Benzo(b)fluoranthene[a]
Fluorene	Benzo(k)fluoranthene[a]
Phenanthrene	Benzo(a)pyrene
Anthracene	Indeno(1,2,3-cd)pyrene[b]
Fluoranthene	Dibenzo(a,h)anthracene[b]
Pyrene	Benzo(g,h,i)perylene

[a] These target analytes coelute.
[b] These target analytes coelute.

The samples were collected on April 12, 1989 and received by the laboratory April 14, 1989. All soil samples were extracted April 15, 1989. All analyses were completed by April 17, 1989.

2.0 FASP METHODOLOGY FOR PAHs

All samples were analyzed as described in FASP Method F060.001. All FASP method QC criteria were met for initial calibration, continuing calibration, final calibration, and quantitation limits.

3.0 FASP DATA

FASP data are not confirmed by mass spectroscopy and, therefore, do not provide the same level of qualitative specificity as CLP data. While FASP data is not equivalent to or a replacement for CLP data, the results presented in this report are consistent (all samples were extracted and analyzed utilizing the same procedure). Data generated by the E & E Seattle Laboratory for the Smith Salvage SSI were used to quantitate site contamination. The FASP analytical quantitation limits were as follows:

Analyte	FQL (µg/kg)
Naphthalene	1,000
Acenaphthylene	1,000
Acenaphthene	1,000
Fluorene	1,000
Phenanthrene	1,000
Anthracene	1,000
Fluoranthene	1,000
Pyrene	1,000
Chrysene	1,000
Benzo(a)anthracene	1,000
Benzo(b)fluoranthene[a]	1,000
Benzo(k)fluoranthene[a]	1,000
Benzo(a)pyrene	1,000
Indeno(1,2,3-cd)pyrene[b]	1,000
Dibenzo(a,h)anthracene[b] 20	
Benzo(g,h,i)perylene	1,000

[a] Coeluting PAHs.
[b] Coeluting PAHs.

3.1 PAHs SAMPLE ANALYSIS RESULTS

Table 3-1 presents FASP results for PAH samples in water taken from the Smith Salvage site in Jones, Oregon.

Table 3.1

SAMPLE RESULTS, SOIL
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
µg/kg (Wet Weight)

Analyte	Sample ID									
	JHB-1	JHB-2	JHB-3	JHB-4	JHB-5	JHB-6	JHB-7	JHB-8	JHB-9	JHB-10
Naphthalene	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF
Acenaphthylene	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF
Acenaphthene	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF
Fluorene	100 UF	100 UF	100 UF	94 F	100 UF	150 F	100 UF	46 F	34 F	100 UF
Phenanthrene	100 UF	9,100F	100 UF	2,900F	100 UF	8,100F	570 F	100 UF	300 F	100 UF
Anthracene	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	260 F	4,350F	8,500F
Fluoranthene	2,670F	12,900F	1,200F	1,610F	670 F	3,570F	370 F	1,990F	2,800F	12,000F
Pyrene	2,090F	16,800F	1,830F	1,810F	580 F	2,100F	660 F	3,000F	4,300F	9,900F
Chrysene	3,200F	15,000F	1,900F	1,900F	590 F	3,200F	1,100F	2,700F	5,100F	11,000F
Benzo(a)anthracene	3,550F	17,200F	1,950F	2,000F	590 F	3,620F	1,640F	2,550F	5,780F	14,000F
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	6,770F	14,500F	1,460F	1,380F	370 F	3,030F	470 F	1,410F	3,500F	12,100F
Benzo(a)pyrene	5,150F	10,700F	2,050F	1,740F	2,840F	300 F	1,600F	2,070F	3,180F	8,460F
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF
Benzo(g,h,i)perylene	4,150F	13,300F	1,600F	1,510F	640 F	500 UF	850 F	1,000F	810 F	12,000UF

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

QC data for this group of samples includes:

Blank = MB-1
Spike = JHB-5(spike)
Duplicate= JHB-7(duplicate)

3.2 PAH QC DATA

1) Method Blank Results

Table 3-2 presents FASP QC data for sample blanks (in soil) made for the Smith Salvage Site in Jones, Oregon.

Table 3-2

METHOD BLANK RESULTS, SOIL
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
(µg/kg, Wet Weight)

Sample ID/Analyte	Method Blank - Soil
Naphthalene	100 UF
Acenaphthylene	100 UF
Acenaphthene	50 UF
Fluorene	100 UF
Phenanthrene	100 UF
Anthracene	100 UF
Fluoranthene	100 UF
Pyrene	100 UF
Chrysene	100 UF
Benzo(a)anthracene	100 UF
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	100 UF
Benzo(a)pyrene	100 UF
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	500 UF
Benzo(g,h,i)perylene	500 UF

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

2) Matrix Spike Results

Table 3-3 presents FASP QC data for PAH matrix spike samples in soil taken from the Smith Salvage site in Jones, Oregon.

Table 3-3

MATRIX SPIKE RECOVERY RESULTS, SOIL
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
(µg/kg, Wet Weight)

Sample ID/Analytes	Amount Spiked	Sample	Sample with Spike	Percent Recovery
Acenaphthylene	1,000	100 F	500 F	60
Acenaphthene	1,000	100 UF	590 F	59
Fluorene	1,000	100 UF	810 F	81
Phenanthrene	1,000	100 UF	800 F	80
Anthracene	1,000	100 UF	790 F	79
Fluoranthene	1,000	670 F	1,510 F	84
Pyrene	1,000	580 F	1,720 F	114
Chrysene				
Benzo(a)anthracene	1,000	590 F	1,480 F	89
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	1,000	370 F	1,500 F	113
Benzo(a)pyrene	1,000	2,840 F	3,710 F	91
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	2,000	500 F	1,920 F	96
Benzo(g,h,i)perylene	2,000	640 F	2,190 F	78

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

3) Duplicate Results

Table 3-4 presents FASP QC data for sample duplicates in soil taken from the Smith Salvage site in Jones, Oregon.

Table 3-4

DUPLICATE RESULTS, SOIL
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
(µg/kg, Wet Weight)

Sample ID/Analytes	Sample Result	Duplicate Result	Relative Percent Difference
Acenaphthylene	100 UF	100 UF	0
Acenaphthene	100 UF	100 UF	0
Fluorene	100 UF	100 UF	0
Phenanthrene	572 F	774 F	30
Anthracene	100 UF	100 UF	0
Fluoranthene	365 F	335 F	8.6
Pyrene	661 F	469 F	34
Chrysene	1,230 F	1,410 F	14
Benzo(a)anthracene	1,630 F	1,360 F	18
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	469 F	325 F	36
Benzo(a)pyrene	1,590 F	1,260 F	23
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	500 UF	500 UF	0
Benzo(g,h,i)perylene	862 F	962 F	11

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.
F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

DRAFT

FASP STANDARD OPERATING GUIDELINE

Polycyclic Aromatic Hydrocarbons (PAHs) In Water

Method F060.002

December 1989

DISCLAIMER

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1.0 SCOPE, APPLICATION, AND LIMITATIONS

1.1 PURPOSE

This Field Analytical Support Project (FASP) method is proposed for use in determining the relative concentrations of various polycyclic aromatic hydrocarbons (PAHs) in water samples.

1.2 LIST OF COMPOUNDS

Table 1-1 lists the compounds that may be determined by this method and approximate method quantitation limits.

1.3 USER RESTRICTIONS

The method should be used only by trained analysts under the supervision of an experienced Chemist.

1.4 ANALYTES IDENTIFIED

The method yields tentative identification and estimated quantitation of the analytes listed in Table 1-1. Report values are on an as received basis.

1.5 VERIFICATION

The primary objective of FASP is to provide analytical data in a timely manner for guidance of ongoing work in the field. Identification of specific target compounds and prior knowledge regarding potential matrix interferences are prerequisites to successful use of FASP. FASP is not equivalent to or a replacement for Contract Laboratory Program (CLP) Analyses. Verification of data through the CLP, encompassing the range of sample concentrations, is recommended.

1.6 QUALITY CONTROL

This FASP SOG should be used in conjunction with FASP SOGs for quality control (QC)--General Quality Control (F030.001), Quality Control-Gas Chromatographic Organic Compound Analyses (F030.002) and Laboratory Safety (F020.001).

Table 1-1

FASP TARGET COMPOUND LIST (FTCL) AND FASP QUANTITATION LIMITS (FQL)[a]

PAH	CAS NUMBER	Quantitation Limits in Water (µg/L)
Naphthalene	91-20-3	20
Acenaphthylene	208-96-8	20
Acenaphthene	83-32-0	20
Fluorene	86-73-7	20
Phenanthrene	85-01-8	20
Anthracene	120-12-7	20
Fluoranthene	206-44-0	20
Pyrene	129-00-0	20
Chrysene	218-01-9	20
Benzo(a)anthracene	56-55-3	20
Benzo(b)fluoranthene[b]	205-00-2	20
Benzo(k)fluoranthene[b]	207-08-9	20
Benzo(a)pyrene	52-32-8	20
Indeno(1,2,3-cd)pyrene[c]	193-39-5	20
Dibenzo(a,h)anthracene[c]	53-70-3	20
Benzo(g,h,i)perylene	191-24-2	20

[a] Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

b These compounds coelute.

c These compounds coelute.

2.0 SUMMARY OF METHOD

A measured amount of water is placed in a volumetric flask. The sample is extracted twice with a measured volume of methylene chloride. Isolation of target analytes is accomplished by silica gel cleanup of the extract to eliminate interferences (primarily aliphatic hydrocarbons). Analysis is performed using a temperature programmed gas chromatograph (GC) with a megabore capillary column or a packed column, and a flame ionization detector (FID). Identification is based on comparison of retention times between samples and standards. Quantitation is by the external standard method.

3.0 INTERFERENCES

Interferences may be minimized by use of pesticide grade or ultrapure reagents, exhaustive cleanup of glassware, and avoidance of plastic materials in laboratory operations. The analytical system must be demonstrated to be free from contamination under conditions of the analysis by running laboratory reagent blanks.

GC interference by sample carryover may be minimized by use of disposable glassware during sample preparation and b y use of the maximum possible rinse cycle on automatic injection systems, or by thoroughly rinsing syringes used in manual injections.

Interferences coextracted from samples are matrix and site specific. It is possible that cleanups used in either FASP or Regular Analytical Services (RAS) CLP methods may fail to eliminate interferences. Highly specialized CLP Special Analytical Services (SAS) techniques may be required to produce acceptable analytical results.

4.0 APPARATUS AND MATERIALS

4.1 ANALYTICAL SYSTEMS

Listed below are two GC options that meet the requirements of this method. Other GC configurations may be substituted if they meet the method requirements.

1) Gas Chromatograph, Option 1

An analytical system complete with a temperature programmable GC suitable for on-column injection is required and all necessary accessories including injector and detector systems designed or modified to accept the appropriate analytical columns (packed or megabore). The system shall have a data-handling system attached to the detectors that is capable of retention time labeling, relative retention time comparisons, and providing relative and absolute peak height and/or peak area measurements.

1) Column 1 - 1.8 m x 3.0 mm I.D. glass column packed with 3% SP-2250 on 100/120 Supelcoport (Supelco) or equivalent.

2) Column 2 - 1.8 m x 3.0 mm I.D. glass column packed with 3% OV-1 on 100/120 Supelcoport (Supelco) or equivalent.

3) Detector - Flame Ionization Detector (FID) with optional makeup gas supply at the detector's inlet.

4) Gas Supply - The carrier gas and makeup gas (if required) should be ultrapure helium or nitrogen. The flame gases are zero air and ultrapure hydrogen or equivalent. All gases should pass through hydrocarbon traps prior to the GC.

2) Gas Chromatograph, Option 2

An analytical system complete with a temperature programmable GC and all necessary accessories including injector and detector systems designed or modified to accept megabore capillary analytical columns is required. The system shall have a data handling system attached to the detector that is capable of retention time labeling, relative retention time comparisons, and providing peak height and/or peak area measurements.

1) Column - 15 m x 0.53 mm I.D. DB-5 fused silica capillary column (FSCC) (J&W Scientific) or equivalent.

2) Detector - FID using a system with makeup gas supply at the detector's capillary inlet.

3) Gas Supply - The carrier gas and makeup should be ultrapure helium or nitrogen. The flame gases are zero air and ultrapure hydrogen or equivalent. All gases should pass through hydrocarbon traps prior to the GC.

4.2 OTHER LABORATORY EQUIPMENT

1) Glass Wool

Heat at 200°C for 24 hours and store in glass jars with Teflon-lined caps.

2) Screw Cap Culture Tubes

Disposable 16 mm x 150 mm borosilicate glass culture tubes with Teflon-lined phenolic caps for extraction.

3) Disposable Pipets

Pasteur, 6 and 9 inches long.
Giant, 10 mm O.D. x 6 inches long.

4) Spatulas

Stainless steel, micro and semimicro.

5) Microsyringe

10 µL.

6) Balance

Top loading, capable of weighing to 0.01 gm, used to weight samples.

7) Micropipets

10-1,000 µL.

8) Volumetric Pipets/Repipets

0.5, 1.0, 5, 10, and 25 mL.

9) Volumetric Flasks

10, 25, 50, 100 mL.

10) Vortex Mixer

Vortex Genie or equivalent.

11) Centrifuge

Capable of holding 16 mm x 150 mm culture tubes.

12) Amber Storage Bottles

100 and 500 mL.

13) Autosampler Vials

1 or 2 mL with Teflon-lined screw caps.

14) Graduated Centrifuge Tubes

15 mL with ground glass stoppers.

15) Hydrocarbon Traps

Supelpure-HC-Trap or equivalent.

16) Leak Detector

Snoop Liquid, or equivalent, for packed-column operations, and GOW-MAC Gas Leak Detector, or equivalent, for megabore capillary operations.

17) Timer

0 to 10 minute range.

18) Teflon Wash Bottles

500 mL.

19) Chromatographic Data Stamp

Used to record instrument operating conditions.

20) Nitrogen Evaporation System

N-Evap, or equivalent.

21) Laboratory Oven

Capable of maintaining temperatures of 200°C.

4.3 REGION-SPECIFIC INSTRUMENT OPTIONS

Region-specific instrument options are provided in Appendix A of this method.

5.0 REAGENTS

5.1 SOLVENTS

Petroleum ether, pesticide quality, or equivalent.

Methylene Chloride, pesticide quality, or equivalent.

Isooctane, pesticide quality, or equivalent.

5.2 MISCELLANEOUS REAGENTS

1) Reagent Water

Reagent water is defined as water in which an interferent is not observed at the FASP Quantitation Limit (FQL) of the analyte of interest. Reagent water may be generated using a carbon filter bed containing activated carbon (Calgon Corporation, Filtrasorb-300 or equivalent) or a water purification system (Milli-Q Plus with Organex Q cartridge or equivalent).

2) Sodium Sulfate

Reagent, anhydrous, granular. The sodium sulfate is reconditioned by heating for 24 hours at 200°C and storing in clean glass containers with Teflon-lined covers.

3) Silica Gel

Grade 923, mesh 100/200. Activate the gel for 16 hours at 130°C in a shallow glass tray loosely covered with foil. The gel may be stored for up to 1 week in glass jars with Teflon-lined covers.

5.3 GASES

1) Helium

Ultrapure or chromatographic grade (always used in conjunction with a hydrocarbon trap).

2) Nitrogen

Ultrapure or chromatographic grade (always used in conjunction with a hydrocarbon trap).

3) Zero Air

Zero grade or chromatographic grade (always used in conjunction with a hydrocarbon trap).

4) Hydrogen

Ultrapure or chromatographic grade (always used in conjunction with a hydrocarbon trap).

5.4 STOCK STANDARD SOLUTIONS

Stock standard solutions of analytes should be purchased as manufacturer certified solutions. Single PAH standards may be used; however, standard mixtures of PAHs are recommended.

5.5 CALIBRATION STANDARDS

Prepare calibration standards at a minimum of three concentration levels for each analyte of interest. This is done through volumetric dilution of the stock standards with isooctane. The lowest concentration standard should be approximately two times the FQL as listed in Table 1-1. The remaining standard concentrations should define the approximate working range of the GC: one at the upper linear range and the other midway between it and the lowest standard. All standards must be stored at 4°C in Teflon-sealed glass bottles. Calibration solutions must be replaced after 6 months, or whenever comparison with check standards indicates a problem.

5.6 CHECK STANDARDS

Check standards are calibration standards independently prepared by a chemist other than the calibration standard preparer.

5.7 MATRIX SPIKE SOLUTIONS

Matrix spike solutions should be prepared by dilution of stock standard solutions so that no more than 250 µL of spike solution is required to provide a final sample spike level within FASP QC limits

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples should be collected, handled, preserved, and shipped maintaining a chain-of-custody following current EPA regulations and recommendations in force at the time of sample collection. The sole exceptions to this rule are the sample volumes required by the laboratory. Water samples should be shipped in 1-liter narrow-mouthed glass containers with Teflon-lined caps.

The use of chain-of-custody records as described in the U.S. EPA "CLP Users Guide" (9240.0-1), December 1988, is required for sample tracking. The maximum holding times for water PAH samples are 7 days between collection and extraction, and 40 days between extraction and analysis.

7.0 CALIBRATION

7.1 INITIAL CALIBRATION

After an experienced chromatographer has ensured that the entire chromatographic system is functioning properly; i.e., conditions exist such that resolution, retention times, response reporting, and interpretation of chromatographic spectra are within acceptable quality control limits, the GC may be calibrated (Section 11). Using at least three calibration standards for each PAH target analyte prepared as described in Section 5.10, initial calibration curves (response versus mass of standard injected) are generated for each PAH target analyte (refer to Section 10 for chromatographic procedures).

The percent relative standard deviation (%RSD, see Section 11) based on each PAH target analyte's three Calibration Factors (CFs, see Section 11) is computed to determine the acceptability (linearity) of the curve. Unless otherwise specified the %RSD must be $\leq$ 25 percent or the calibration is invalid and must be repeated. Any time the GC system is altered (e.g., new column, or change in gas supply, change in oven temperature) or shut down, a new initial calibration curve must be established.

7.2 CONTINUING CALIBRATION

The GC system is rechecked on a regular basis through the continuing calibration. The midrange initial calibration standard is generally the most appropriate choice for continuing calibration validation. This single point analysis follows the same analytical procedures used in the initial calibration. Instrument response is used to compute the CF, which is then compared to the mean initial calibration factor (CF), and a relative percent difference (RPD, see Section11) is calculated. Unless otherwise specified, the RPD must be $\leq$ 25 percent for the continuing calibration to be considered valid. Otherwise, the calibration must be repeated. A continuing calibration remains valid for a maximum of 24 hours providing the GC system remains unaltered during that time.

The continuing calibration is used in all target analyte sample concentration calculations (Section 11) for the period over which the calibration has been validated.

7.3 FINAL CALIBRATION

The final calibration must be obtained at the end of each batch of sample analyses. The maximum allowable RFD between the mean initial calibration and the final calibration factors for each analyte must be $\leq$ 50 percent. A final calibration that achieves $\leq$ 25 percent RPD may be used as an ongoing continuing calibration.

8.0 EXTRACTION

The sample extraction technique for PAHs in water is as follows:

1) Add 100 mL of water to clean 100 mL volumetric flask.

2) Add 3.0 mL methylene chloride by repipet to the flask and shake vigorously for 2 minutes.

3) Allow the layers to separate.

4) Transfer the organic layer to a 10-mL graduated centrifuge tube using a disposable pasteur pipet.

5) Repeat steps 2 through 4 twice and combine the extracts.

6) Add a small quantity of anhydrous sodium sulfate to the extract and vortex for 30 seconds.

7) Add 2 mL of isooctane and vortex for 10 seconds.

8) Reduce the solvent volume to approximately 1.0 mL with gentle heat under a N_2 stream.

9) Extract ready for cleanup.

9.0 CLEANUP

The use of a silica gel chromatography column as part of a routine cleanup procedure may not be necessary in all cases, but is required for all samples as a general precaution. Clean extracts extend both column and detector life, and provide more accurate and precise data. Technique gained through experience is critical in column chromatography. Columns must not be allowed to lose their slurry characteristics, or channeling may significantly reduce cleanup effectiveness. Mixing between solvents must be minimized to avoid poor chromatographic separations.

9.1 SILICA GEL COLUMN PREPARATION

1) Place a small slug of muffle-furnaced glass wool into a 10 mm O.D. (4 mL) giant pipet.

2) Add 1.8 g of activated silica gel to the column.

3) Add a 1 cm layer of anhydrous sodium sulfate on top of the silica gel.

4) Rinse the column with 10 mL of methylene chloride and discard the rinsate. From this point on, the column must <u>not</u> be allowed to go dry until the cleanup is completed.

5) Rinse the column with 10 mL of petroleum ether and discard the rinsate.

9.2 GENERAL EXTRACT CLEANUP

<u>Extract Cleanup</u>

1) Add the concentrated sample extract (Section 8) to the column using a small disposable pipet.

2) Rinse the extract culture tube with two 0.5 mL aliquots of isooctane and add the rinsate to the column.

3) Elute the column with 6.0 mL of petroleum ether and discard the solvent.

4) Elute the column with 10 mL of methylene chloride. Collect the first 10 mL of eluted solvent in a graduated centrifuge tube.

5) For highly contaminated samples, the extract is now ready for GC injection. However, in most cases, greater sensitivity is required and is achieved by proceeding as follows:

6) Reduce the solvent volume to less than 1 mL with low heat under a nitrogen stream.

7) Stopper the centrifuge tube and allow to cool. Record the volume.

8) The sample extract is now ready for GC injection.

9.3 SOLID PHASE EXTRACTION TECHNOLOGY

Solid phase extraction (SPE) technology (e.g., Sep-Pak) may provide an acceptable alternative to acid cleanup for PAH extracts if method validation studies are conducted to provide evidence of their utility. However, in-house testing has shown blank contamination from SPE materials prohibits their use.

9.4 CLP RAS/SAS ANALYSES

FAST methodologies, including cleanup, may not be sufficient to continue acceptable analyses. In such cases, CLP RAS/SAS analyses be the only acceptable alternatives.

10.0 INSTRUMENTAL ANALYSIS

10.1 INSTRUMENT PARAMETERS

Table 10-1 summarizes an example of acceptable instrument operating conditions for the GC. Other instruments, columns, and/or chromatographic conditions may be employed if FAST QC criteria are met.

Table 10-1

EXAMPLE FASP GC OPERATING CONDITIONS

Instrument:	Shimadzu GC-14A equipped with FID modified to accept megabore capillary columns.
Integrator:	Shimadzu Chromatopac C-R4A Data Processor.
Column:	J&W 15 m x 0.53 mm DB-5 fused silica megabore capillary column.
Carrier Gas:	Ultrapure Helium or Nitrogen, at a flowrate of 10 mL/min.
Detector Gas:	Zero air at a flowrate of 300 mL/min; ultrapure hydrogen at a flowrate of 40 mL/min.
Column (oven) Temperature Program:	Initial temperature: 75°C for 2 mins. Ramp at 15°C/min. Final temperature: 310°C for 7 mins.
Injector Temperature:	330°C.
Detector Temperature:	330°C.
GC Analysis Time:	Approximately 25 mins.
Standard/ Sample Injection:	Solvent flush manual injection or automated sample injection is recommended for PAH analysis. Two microliters of nanograde methylene chloride, 0.5 µL of air, and 2.0 and 3.0 µL (measured to the nearest 0.05 µL) of sample extract are sequentially drawn into a 10-µL syringe and immediately injected into the GC.

10.2 CHROMATOGRAMS

Computer reproduction of chromatograms that are attenuated to ensure all peaks are on scale over a 100-fold range are acceptable. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Generally, peak response should be > 25 percent and < 100 percent of full-scale deflection to allow visual recognition of the various PAH compounds.

The following information must be recorded on each chromatogram.

1) Instrument and detector identification;
2) Column packing, coating, length, and I.D.;
3) Oven temperature;
4) Injector/detector temperature;
5) Gas and flow;
6) Site name;
7) Sample number;
8) Date and time; and
9) GC operator initials.

10.3 PAH IDENTIFICATION

Qualitative identification of PAHs is based on retention time as compared to standards on a single column. A second, dissimilar column may be used to assist in identification.

Generally, individual peak retention time windows should be ≤ 2 percent for megabore capillary columns (≤ 5 percent for packed columns.

It may not be possible or practical to separate all target analyte PAHs on a single column. In such cases these target analytes should be denoted as the appropriate combination of PAHs.

It is possible that interferences may preclude positive identification of an analyte. In such cases, the chemists should report the presence of the interferents with the maximum possible PAH concentration (see Section 9 and 11.4).

10.4 REGION-SPECIFIC INSTRUMENT PARAMETERS

Specific instrument operating parameters are provided in Appendix B of this method.

10.5 ANALYTICAL SEQUENCE

1) Instrument blank.
2) Initial calibration
3) Check standard solution and/or performance evaluation sample (if available).
4) Continuing calibration; repeat within 24 hours of previous continuing calibration.
5) Associated QC lot method blank.
6) Twenty samples and associated QC lot spike and duplicate.

7) Repeat sequence beginning at Step 5 until all sample analyses are completed or another continuing calibration is required.

8) Final calibration when all sample analyses are complete.

11.0 CALCULATIONS

11.1 INITIAL CALIBRATION

Chromatographic response to PAH target analytes is measured by determining Calibration Factors (CFs). In the case of coeluted analytes, the summed areas and masses should be employed to generate a combined CF for the target analyte PAHs. Calculate the CF for each PAH target analyte in the initial standard. The integrator may be used to make all of these computations.

$$CF = \frac{\text{Area of Peak}}{\text{Mass Injected (in nanograms)}}$$

Using the calibration factors, calculate the percent relative standard deviation (%RSD) for each PAH at a minimum of three concentration levels using the following equation.

$$\%\ RSD = \frac{SD}{\bar{X}} \times 100$$

where SD. the Standard Deviation, is given by

where: X_i = individual calibration factor (per analyte),
$\bar{X}$ = mean of initial three calibration factors (per analyte),
N = number of calibration standards.

The %RSD must be ≤ 25.0 percent.

11.2 CONTINUING CALIBRATION

Sample quantitation is based on analyte calibration factors calculated from continuing calibrations. Midrange standards for all initial calibration PAH target analytes must be analyzed at specified intervals (≤ 24 hours).

The maximum allowable relative percent difference (RPD) calculated using the equation below for each analyte must be ≤ 25 percent.

where: CF_I = mean CF from the initial calibration for each analyte
CF_C = measured CF from the continuing calibration for the same analyte

11.3 FINAL CALIBRATION

The final calibration is obtained at the end of any batch of samples analyzed.

The maximum allowable RPD between the mean initial calibration and final calibration factors for each PAH target analyte must be ≤ 50 percent. A final calibration that achieves ≤ 25 percent RPD may be used as an ongoing continuing calibration.

where: CF_I = mean CF from the initial calibration for each analyte
CF_F = final CF for the same analyte

11.4 SAMPLE QUANTITATION

Calculate the concentration in the sample using the following equation for external standards. The response can be measured by automated peak height or peak area measurements from an integrator. Sample quantitation is based on analyte calibration factors calculated from continuing calibrations.

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(CF_c)(V_i)(V_s)}$$

where: A_x = response for the analyte to be measured

CF_c = CF from the continuing calibration for the same analyte

V_i = volume of extract injected (μL)

V_t = volume of total extract (μL)

V_s = volume of water extracted (μL)

D = dilution factor if employed

Report results in micrograms per liter ($\mu g/L$) without correction for blank or spike recovery.

Coeluted analytes should be quantitated and reported as the combination of the unseparated PAH target analytes.

Sample spectra may not match identically with those of analytical standards. When positive identification is questionable, the chemist may calculate and report a maximum possible concentration (flagged as ≤ the numerical value) that allows the data user to determine if additional (e.g., CLP RAS or SAS) work is required or if the reported concentration is below action levels and project objectives and DQOs have been met, to forego further analysis.

Similarly, when sample concentration exceeds the linear range, the analyst may report a probable minimum level (flagged as > the numerical value) which allows the data user to determine if additional (e.g., CLP RAS or SAS) work is required, or--if the reported concentration is above action levels and project objectives and DQOs have been met--to forego further analysis.

QC criteria (as described in FASP QC SOGs) must be met for all analyses. Advisory limits for spike %R and duplicate RPD are presented in Table 11-1.

Table 11-1

FASP MATRIX SPIKE PERCENT RECOVERY (%R) AND DUPLICATE RELATIVE PERCENT DIFFERENCE (RPD) ADVISORY WATER QC LIMITS METHOD F060.002 (PAHs IN WATER)

Analyte	FASP Advisory Quality Control Limits[a]	
	Spike %R (%)	Duplicate RPD (%)
Naphthalene	30 - 200	± 100
Acenaphthylene	30 - 200	± 100
Acenaphthene	30 - 200	± 100
Fluorene	30 - 200	± 100
Phenanthrene	30 - 200	± 100
Anthracene	30 - 200	± 100
Fluoranthene	30 - 200	± 100
Pyrene	30 - 200	± 100
Benzo(a)anthracene	30 - 200	± 100
Chrysene	30 - 200	± 100
Benzo(b)fluoranthene[b]		
Benzo(k)fluoranthene[b]	30 - 200	± 100
Benzo(a)pyrene	30 - 200	± 100
Indeno(1,2,3-cd)pyrene[c]		
Dibenzo(a,h)anthracene[c]	30 - 200	± 100
Benzo(g,h,i)perylene	30 - 200	± 100

[a] If the concentration of an FTCL analyte is less than five times the FQL, FASP advisory control limits for duplicate RPD values become ±3 times the FQL for that individual analyte.

[b] Coeluting analytes.

[c] Coeluting analytes.

12.0 METHOD PERFORMANCE

The following chromatogram is an example of a chromatogram for several commonly encountered PAHs.

12.1 GAS CHROMATOGRAM - PAH COMPOUNDS

Column: 15 m x 0.53 mm DB-5 fused silica megabore capillary

Column Temperature Program: Initial 75°C - 2 mins; ramp 15°C per minute; final 310°C - 7 mins

Detector/Injector Temperature: 330°C

Carrier Gas: Helium at 10 mL/min

Detector: FID

12.2 Method F060.002 EXAMPLES OF QA/QC RESULTS

Spike triplicate, and split sample results are presented as examples of FASP Method F060.002 empirical data in Tables 12-1, 12-2, and 12-3, respectively.

Table 12-1

FAST METHOD F060.002
WATER MATRIX SPIKE PERCENT RECOVERY (%R)

Analyte	Number of Samples	%R
Acenaphthylene	1	57
Acenaphthene	1	55
Fluorene	1	86
Phenanthrene	1	112
Anthracene	1	141
Fluoranthene	1	64
Pyrene	1	32
Benzo(a)anthracene	1	113
Chrysene	1	113
Benzo(b)fluoranthene/ Benzo(k)fluoranthene	1	111
Benzo(a)pyrene	1	173
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	1	142
Benzo(g,h,i)perylene	1	107

13.0 DELIVERIES

13.1 VERBAL SUMMARIES OF SAMPLE RESULTS

A verbal summary of sample results should be available within 24 hours of sample analysis by the laboratory or a facsimile type hard copy via telecommunication may be substituted. If computer compatibility can be established, a modem link may be used to transfer data from the laboratory to field personnel.

13.2 FINAL FAST REPORT

The final FASP report generated for each project should include the following:

1) A reference to the FASP method used and a note addressing any changes to method.

2) A hard copy of all data and summary sheets documenting required QA/QC data (available within 14 days of completion of all FASP analyses for a project).

3) A data summary of all reportable results with units ug/kg clearly specified.

4) All calculations using standard good measurement practices in the use of significant figures. Rounding off will be allowed only for final deliverable values.

5) All sample results will be reported using two significant figures. QC data will be reported in three significant figures.

6) A statement by analyte that initial, continuing, and final CFs, %RSDs, and RPDs FAST QC were met.

7) A summary table of the blank, matrix spike, and duplicate results for each target analyte.

8) A summary of FQLs for each target analyte is also a final deliverable requirement.

9) A comparison of interlaboratory split sample results should be submitted as an addendum to the final FASP report.

Again, all results must be annotated (followed by the flag, F) by the laboratory to indicate to future data users that FASP techniques were used in sample analysis.

13.3 EXAMPLE FINAL REPORT

An example of a standard reporting format is provided in Appendix C of this method.

14.0 SAMPLE AND DATA STORAGE

14.1 DISPOSAL OF SAMPLES

Samples should be disposed of in accordance with established Federal, State, and local regulations and policies after a minimum holding period of 14 days after receipt by the laboratory. Sample extracts may be disposed of 30 days after final FASP report submission.

14.2 RAW AND SUMMARY DATA STORAGE

The lab must maintain a hard copy or computer disk storage of all raw (including instrument printouts and logbooks) and summary data associated with an analytical case for a minimum of 6 months after receipt of the hard copy report by the data user.

14.3 PERMANENT DATA STORAGE

After the 6-month period has elapsed, the laboratory should place all records, including laboratory notebooks, into permanent storage (TDD/PAN files).

APPENDIX A

FASP METHOD F060.002

E & E Region X FIT Instrument Options

GC System - Shimadzu GC-mini 2 with FID modified with a Direct Conversion and Makeup Gas Adapter for megabore capillary column operations.

Temperature Programmer - Shimadzu TP-M2R for temperature-programmed megabore capillary column analyses.

Date Handling System 1 - Shimadzu Data Processor Chromatopac C-RIB.

Data Handling System 2 - Shimadzu Data Processor Chromatopac C-R3A.

Data Handling System 3 - Shimadzu Data Processor Chromatopac C-R3A equipped with a CRT display unit and Shimadzu FDD-1A Floppy Disk Drive.

Data Handling System 4 - P.E. Nelson 2100 SW Integrator with 960 Series Intelligent Interface, Hyundai 80286 computer, and Epson LX800 printer.

APPENDIX B

FASP METHOD F060.002

E & E Region X FIT Instrument Parameters

Instrument: Shimadzu GC Mini-2 equipped with FID modified to accept megabore capillary columns and Shimadzu TP-M2R temperature programmer.

Integrator: Shimadzu Chromatopac C-R3A Data Processor.

Columns: J&W 15 m x 0.53 mm DB-5 fused silica megabore capillary column or Supelco 30 m x 0.75 mm SPB-5 borosilicate megabore capillary column.

Carrier Gas: Ultrapure helium or nitrogen, 10 mL/min.

Detector Gas: Zero air, 300 mL/min; ultrapure hydrogen, 40°C mL/min.

Column (Oven) Temperature: Initial temperature 75°C for 2 min. Ramp 15°C/min. Final temperature 310°C for 7 min.

Injector Temperature: 330°C.

Detector Temperature: 330°C.

APPENDIX C

FASP METHOD F060.002

EXAMPLE FINAL REPORT

October 1991

MEMORANDUM

DATE: May 18, 1999

TO: John White, FIT-RPO, US EPA Region X

THRU: Jeffrey Yellow, FIT-OM, E & E, Seattle

FROM: Tracy Red, Senior Chemist, E & E, Seattle

SUBJ: FASP Polycyclic Aromatic Hydrocarbon (PAH) Analytical Results
Smith Salvage
Jones, Oregon

REF: TDD F10-8903-100
PAN FOR0999SC

CC: Andrew Orange, FIT-RFC, E & E, Seattle
Gerald Black, DPO, US EPA, Region XX
Bruce Blue, ESD, US EPA, Region XX
Hunt Green, FASP-PM, E & E, Arlington

Transmitted herewithin are the results for the PAH analyses 10 samples from the Smith Salvage Site, Jones, Oregon.

TY:csr

Enclosures

October 1991

FASP POLYCYCLIC AROMATIC HYDROCARBON ANALYTICAL RESULTS

SMITH SALVAGE
JONES, OREGON

TDD F10-8903-100
PAN FORO999SC

Investigation Date: April 1999

FIT Analytical Team: Tracy Red and David Tan

Report Date: May 1999

Submitted to: John E. White, Regional Project Officer
Field Operations and Technical Support Branch
U.S. Environmental Protection Agency
Region XX
Seattle, Washington

DISCLAIMER

This report has been prepared by Ecology and Environment, Inc. (E & E), under EPA Contract 68-01-7347. It has been reviewed and approved for public release by the U.S. Environmental Protection Agency (EPA). Mention of commercial products does not constitute endorsement by the U.S. Government. Technical content of this report is the responsibility of E & E, Seattle, Washington, and does not necessarily reflect the views or policies of the EPA.

1.0 INTRODUCTION

Analysis of 10 water samples, collected at the Smith Salvage Site, was performed by Ecology and Environment, Inc. (E & E) Field Investigation Team (FIT) Chemists under Technical Directive Document (TDD) F10-8903-100, utilizing the E & E base laboratory in Seattle, Washington. The samples were analyzed for polycyclic aromatic hydrocarbons (PAHs) to acquire analytical data as an integral part of a Screening Site Inspection (SSI). In additional, three quality control samples were analyzed to monitor analytical method performance and to ensure data validity.

Samples were analyzed using the Standard Operating Guidelines for the Field Analytical Support Project FASP Method F060.002. As required by the USEPA, FASP data are annotated with the data qualifier "F" indicating that FASP methodologies were used to generate the data. As such, qualitative data are defined as tentatively identified and quantitative data should be interpreted as estimated quantities.

Samples were analyzed for the following PAHs:

Naphthalene	Chrysene
Acenaphthylene	Benzo(a)anthracene
Acenaphthene	Benzo(b)fluoranthene[a]
Fluorene	Benzo(k)fluoranthene[a]
Phenanthrene	Benzo(a)pyrene
Anthracene	Indeno(1,2,3-cd)pyrene[b]
Fluoranthene	Dibenzo(a,h)anthracene[b]
Pyrene	Benzo(g,h,i)perylene

[a] These target analytes coelute
[b] These target analytes coelute

The samples were collected on April 12, 1989 and received by the laboratory April 14, 1989. All water samples were extracted April 15, 1989. All analyses were completed by April 17, 1989.

2.0 FASP METHODOLOGY FOR PAHs

All samples were analyzed as described in FASP Method F060.002. All FASP method QC criteria were met for initial calibration, continuing calibration, final calibration, and quantitation limits.

3.0 FASP DATA

FASP data are not confirmed by mass spectroscopy and, therefore, do not provide the same level of qualitative specificity as CLP data. While FASP data is not equivalent to or a replacement for CLP data, the results presented in this report are consistent (all samples were extracted and analyzed utilizing the same procedure). Data generated by the E & E Seattle Laboratory for the Smith Salvage SSI were used to quantitate site contamination. The FASP analytical quantitation limits were as follows:

Analyte	FQL (µg/L)
Naphthalene	20
Acenaphthylene	20
Acenaphthene	20
Fluorene	20
Phenanthrene	20
Anthracene	20
Fluoranthene	20
Pyrene	20
Chrysene	20
Benzo(a)anthracene	20
Benzo(b)fluoranthene[a]	20
Benzo(k)fluoranthene[a]	20
Benzo(a)pyrene	20
Indeno(1,2,3-cd)pyrene[b]	20
Dibenzo(a,h)anthracene[b] 20	
Benzo(g,h,i)perylene	20

[a] Coeluting PAHs.
[b] Coeluting PAHs.

3.1 PAHs SAMPLE ANALYSIS RESULTS

Table 3-1 presents FASP results for PAH samples in water taken from the Smith Salvage site in Jones, Oregon.

Table 3.1

SAMPLE RESULTS, WATER
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
µG/L

Analyte	Sample ID									
	JHB-1	JHB-2	JHB-3	JHB-4	JHB-5	JHB-6	JHB-7	JHB-8	JHB-9	JHB-10
Naphthalene	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF
Acenaphthylene	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF
Acenaphthene	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF	50 UF
Fluorene	100 UF	100 UF	100 UF	94 F	100 UF	150 F	100 UF	46 F	34 F	100 UF
Phenanthrene	100 UF	9,100F	100 UF	2,900F	100 UF	8,100F	570 F	100 UF	300 F	100 UF
Anthracene	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	100 UF	260 F	4,350F	8,500F
Fluoranthene	2,670F	12,900F	1,200F	1,610F	670 F	3,570F	370 F	1,990F	2,800F	12,000F
Pyrene	2,090F	16,800F	1,830F	1,810F	580 F	2,100F	660 F	3,000F	4,300F	9,900F
Chrysene	3,200F	15,000F	1,900F	1,900F	590 F	3,200F	1,100F	2,700F	5,100F	11,000F
Benzo(a)anthracene	3,550F	17,200F	1,950F	2,000F	590 F	3,620F	1,640F	2,550F	5,780F	14,000F
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	6,770F	14,500F	1,460F	1,380F	370 F	3,030F	470 F	1,410F	3,500F	12,100F
Benzo(a)pyrene	5,150F	10,700F	2,050F	1,740F	2,840F	300 F	1,600F	2,070F	3,180F	8,460F
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF	500 UF
Benzo(g,h,i)perylene	4,150F	13,300F	1,600F	1,510F	640 F	500 UF	850 F	1,000F	810 F	12,000UF

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

QC data for this group of samples includes:

Blank = MB-1
Spike = JHB-5(spike)
Duplicate= JHB-7(duplicate)

3.2 PAH QC DATA

1) Method Blank Results

Table 3-2 presents FASP QC data for PAH blank samples (in water) made for the Smith Salvage Site in Jones, Oregon.

Table 3-2

METHOD BLANK RESULTS, WATER
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
(µg/L)

Sample ID/Analyte	Method Blank - Water
Naphthalene	20 UF
Acenaphthylene	20 UF
Acenaphthene	20 UF
Fluorene	20 UF
Phenanthrene	20 UF
Anthracene	20 UF
Fluoranthene	20 UF
Pyrene	20 UF
Chrysene	20 UF
Benzo(a)anthracene	20 UF
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	20 UF
Benzo(a)pyrene	20 UF
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	20 UF
Benzo(g,h,i)perylene	20 UF

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

2) Matrix Spike Results

Table 3-3 presents FASP QC data for PAH matrix spike samples in water taken from the Smith Salvage site in Jones, Oregon.

Table 3-3

MATRIX SPIKE RECOVERY RESULTS, WATER
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
(μg/L)

Sample ID/Analytes	Amount Spiked	Sample	Sample with Spike	Percent Recovery
Acenaphthylene	1,000	100 F	500 F	60
Acenaphthene	1,000	100 UF	590 F	59
Fluorene	1,000	100 UF	810 F	81
Phenanthrene	1,000	100 UF	800 F	80
Anthracene	1,000	100 UF	790 F	79
Fluoranthene	1,000	670 F	1,510 F	84
Pyrene	1,000	580 F	1,720 F	114
Chrysene				
Benzo(a)anthracene	1,000	590 F	1,480 F	89
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	1,000	370 F	1,500 F	113
Benzo(a)pyrene	1,000	2,840 F	3,710 F	91
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	2,000	500 F	1,920 F	96
Benzo(g,h,i)perylene	2,000	640 F	2,190 F	78

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

3) Duplicate Results

Table 3-4 presents FASP QC data for PAH duplicate samples taken from the Smith Salvage site in Jones, Oregon.

Table 3-4

DUPLICATE RESULTS, WATER
POLYCYCLIC AROMATIC HYDROCARBON FASP ANALYSIS
SMITH SALVAGE, JONES, OREGON
(µg/L)

Sample ID/Analytes	Sample Result	Duplicate Result	Relative Percent Difference
Acenaphthylene	100 UF	100 UF	0
Acenaphthene	100 UF	100 UF	0
Fluorene	100 UF	100 UF	0
Phenanthrene	572 F	774 F	30
Anthracene	100 UF	100 UF	0
Fluoranthene	365 F	335 F	8.6
Pyrene	661 F	469 F	34
Chrysene	1,230 F	1,410 F	14
Benzo(a)anthracene	1,630 F	1,360 F	18
Benzo(k)fluoranthene/ Benzo(b)fluoranthene	469 F	325 F	36
Benzo(a)pyrene	1,590 F	1,260 F	23
Indeno(1,2,3-cd)pyrene/ Dibenzo(a,h)anthracene	500 UF	500 UF	0
Benzo(g,h,i)perylene	862 F	962 F	11

U - The material was analyzed for but was not detected. The associated numerical value is a FASP quantitation limit, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

APPENDIX C
STANDARD OPERATING GUIDELINES FOR THE ANALYSIS OF METALS THROUGH X-RAY FLUORESCENCE

DRAFT

FIELD ANALYTICAL SUPPORT PROJECT STANDARD OPERATING GUIDELINE

Metals Analysis by X-Ray Fluorescence in Soil and Sediment

1.0 SCOPE, APPLICATION, AND LIMITATIONS

The following sections present the purpose of the Field Analytical Support Project (FASP), standard operating guideline (SOG), a list of compounds to be identified by the FASP, user restrictions, data verification methods, and FASP SOG quality control (QC) methods.

1.1 PURPOSE

This FASP SOG for metal analysis by x-ray fluorescence is proposed for use in determining the concentrations of various metals in soil and sediment samples. The primary objective of the FASP SOG is to provide analytical data in a timely manner to guide ongoing field work.

1.2 LIST OF COMPOUNDS

Table 1-1 lists the compounds that may be identified by the metal analysis method and approximate method quantitation limits.

1.3 USER RESTRICTIONS

The metal analysis method should be used only by a certified x-ray fluorescence technician under the supervision of an experienced chemist.

1.4 DATA VERIFICATION

Identification of specific target compounds and prior knowledge regarding potential matrix interferences are prerequisites to successful use of the FASP analysis method. The FASP analysis method is not equivalent to or a replacement for Contract Laboratory Program (CLP) Analyses. Verification of data through the CLP, encompassing the range of sample concentrations, is recommended.

1.5 QUALITY CONTROL

This FASP SOG should be used in conjunction with the FASP SOGs for quality control (QC -- General Quality Control (F030.001) and Laboratory Safety (F020.001)).

TABLE 1-1

FASP TARGET ANALYTE LIST (FTAL) AND FASP QUANTITATION LIMITS (FQL)[a] FOR METALS IN SOIL

Analyte	CAS Number	Quantitation Limits[b] in Soil and Sediment Samples (micrograms per kilogram µg/kg)
Antimony	7440-36-0	20[c]
Arsenic (As)	7440-38-2	20
Barium (Ba)	7440-39-3	20[c]
Cadmium (Cd)	7440-43-9	20[c]
Cobalt (Co)	7440-48-4	40
Copper (Cu)	7440-50-8	50
Lead (Pb)	7439-92-1	30
Chromium (Cr)	7440-47-3	200
Mercury (Mg)	7439-97-6	30
Nickel (Ni)	7440-02-0	80
Selenium	7782-49-2	20
Silver (Ag)	7440-22-4	30[c]
Thallium	7440-28-0	--[d]
Thorium	7440-29-1	--[d]
Vanadium	7440-62-2	40[e]
Zinc (Zn)	7440-66-6	40

a Specific quantitation limit values are highly matrix-dependent. The quantitation limits listed here are provided for guidance and may not always be achievable.

b Quantitation limits listed for soil and sediment samples are on an as-received basis. Analyses should be performed using cadmium (Cd-109) as the excitation source unless noted.

c Americium (Am-241) is the excitation source.

d Data is not yet available for these elements.

e Iron (Fe-55) is the excitation source.

2.1 SOIL METHOD ANALYSIS

A sufficient amount of soil to evenly cover the thin film (mylar) of the 1.25 inch-diameter polyethylene sample cup will be used for each sample analysis. If samples contain an excess amount of moisture, they will be dried to an equal level before being inserted into the sample chamber. The appropriate excitation source will be selected (Fe-55, Cd-109, or Am-241) depending on the contaminant metals of interest. By exposing the sample to an x-ray excitation source having energy greater than the binding energy of the sample compounds inner shell electrons, the inner shell electrons of each compound element are dislodged. These electron vacancies are filled by electrons cascading in from outer shells. The cascading electrons produce x-rays of characteristic energy levels for each element as the inner vacancies are filled. A qualitative analysis of the samples can be made by observing the characteristic x-rays produced by the sample. The intensity of the characteristic x-ray emitted is proportional to the concentration of the target compounds. The energy and intensity of the x-rays emitted by the samples is detected by a silicon-lithium (SiLi) detector cooled with liquid nitrogen (LN_2). The spectrographic data is reduced and quantified by an on-site portable computer and software. See section 4.0 for more instrument details.

3.0 SAMPLE ANALYSIS INTERFERENCE

Interferences result from overlapping spectra of elements that emit x-rays with similar energy levels (measured in kiloelectron volts; keV). An example is the interference of arsenic (As) (K_α) (10.54 keV) with the lead (Pb) (L_α) (10.55 keV) x-ray spectra. To overcome the potential for these interferences, an alternate energy fluorescence x-ray characteristic of the compound of concern is chosen. For the As - Pb interference, the As (K_β) spectra (11.73 keV) and the Pb (L_β) spectra (12.61 keV) are chosen for analysis and quantification.

4.1 DESCRIPTION OF SEFA-P XRF

The HNU SEFA-P XRF is a full featured portable Multi-Channel Analyzer (MCA) with an SiLi detector. The MCA is battery operated, has dual displays, a 24-key keypad, an integral digital cassette recorder, and features serial input/output through an RS-232-C interface, computational firmware, and an internal programming mode.

The SEFA-P XRF identifies and quantifies chemical elements by energy dispersive

x-ray spectroscopy. A sample is placed in a sample chamber of the SEFA-P XRF, where it is bombarded with gamma rays from a radioactive source installed in the instrument. The sample can be solid, liquid, slurry, or powder, and does not normally require any special preparation for qualitative analysis. The sample must fit into the sample chamber, either with or without a sample holder, and the cover closed. The analysis does not destroy the samples and can be repeated with highly reproducible results.

After the sample has been bombarded with gamma rays and the data collected, the SEFA-P XRF produces a spectral distribution of the characteristic energy lines of all of the sample elements, from sodium to uranium. The relative abundance of each element in the sample can be computed from the accumulated spectral data.

The basic SEFA-P XRF system consists of one main cabinet that encloses the sample chamber, the radioactive source(s), a LN_2-cooled SiLi detector preamplifier (the LN_2 creates low temperature operating ranges for increased detection sensitivity), spectrometer electronics, MCA, and a battery charger. It is approximately 21 inches long, 12 inches wide, 16 inches tall, and weighs less than 50 pounds.

4.1.1 Features

The SEFA-P XRF can accommodate approximately three radioactive sources, hold up to four samples, and also features a battery-powered time and date clock, a data recorder, and RS-232-C PC interface. See figure 4-1 for a front-view diagram of the SEFA-P XRF.

4.1.2 Major System Components

Figure 4-1 shows a front view of the SEFA-P XRF. Main cabinet major components described here include the sample chamber, radioactive source(s), SiLi detector, preamplifier, LN_2 Dewar, MCA, and battery charger.

FIGURE 4-1
SEFA-P XRF ANALYZER, FRONT VIEW

Source: HNU Systems, Inc.

Main Cabinet

A. Interlock/Sample Chamber

A mechanical interlock on the sample changer door protects the operator from being accidentally exposed to radiation from any of the internal radiation sources. The maximum radiation emanating from this enclosure is at such a low level that it should not represent a safety hazard. Access to the sample changer is obtained by rotating the source knob to the Safety position, allowing the chamber door to be slid open. The door to the sample chamber must be closed to enable operation of the knob that controls selection of the radiation source.

Each installed source is identified by a label on the source knob. The knob that selects the radiation source is marked for four settings: ▲I▲; 1; 2; and 3. The knob must be set at ▲I▲ to unlatch the chamber door, and the knob cannot be turned to any of the source selections while the chamber is open. When the chamber is closed, the knob can be rotated to expose the contents of the chamber to the selected radiation source.

The sample chamber accommodates four samples at a time. The chamber can be opened (when the source is shielded from the operator) to permit removal or insection of the samples. The following figure shows the sample chamber. Figure 4-2 shows the procedure for inserting samples into the sample chamber.

B. Radioactive Source(s)

The radioactive source causes the sample to ionize the appropriate electron shell of the compounds present. These following three sources are offered with the SEFA-P XRF:

Isotope	Maximum Activity
Cd-109	10 (mCi)
Fe-55	50 mCi
Am-241	25 mCi

C. Silicon-Lithium (SiLi) Detector

The SiLi detector crystal is the heart of the SEFA-P XRF; its high resolution and low background permit maximum sensitivity in trace metal analysis. The detector is made from very

FIGURE 4-2
INSERTING A SAMPLE INTO THE SAMPLE CHAMBER

Source: HNU Systems, Inc.

pure Si. Li is "deifted" into the Si crystal, resulting in a semiconductor crystal that effectively is without impurities. When an x-ray strikes the detector, electrons in the crystal absorb an amount of energy proportional to the energy of the x-ray, thus converting the x-ray signal to an electronic signal.

D. Preamplifier

The preamplifier collects the electronic signal (in the form of a minute volt pulse) from the detector, amplifies it, and sends it to the MCA.

E. Liquid Nitrogen Dewar

Low temperature of the liquid nitrogen dewar stabilizes the detector crystal as well as allowing the preamplifier to function more efficiently, thus reducing extraneous noise, improving resolution.

F. Multichannel Analyzer (MCA)

The MCA sorts the signals coming from the preamplifier by energy level and counts the number cathode ray tube of x-rays that strike the detector. This data can then be displayed on a cathode ray tube (CRT) or printed. The MCA provides an amplifier, preamplifier power, high voltage, and digital recorder.

The internal battery can power the MCA for 8 hours on a full charge.

The cassette recorder is a simple and reliable way to save data; the built-in cassette recorder only requires a simple key sequence to record the entire spectrum, parameters, and ROI information.

G. Battery Charger

The battery charger is switchable for either 110 or 220 VAC, and has a two-position setting for either battery charging or continuous operation. It is recommended that the internal battery be fully charged before operation. To change the battery, follow the procedures below:

1. Set the line voltage switch on the charger for the proper setting and plug into either a 110 volt or 220 volt AC line source.

2. Place the switch on the charger toward CHARGE BATTERY and plug the cable into the connector marked CHARGER on the MCA. The green (LED) indicates the battery is charging, and the red LED indicates that the power is on. When the green LED is off, the battery is fully charged.

3. Place the switch on the charger toward OPERATE MCA. The charger may be left connected after the MCA is turned on.

4.1.3 Operating Conditions

The following table presents an example of acceptable operating conditions for the HNU SEFA-P XRF. Other instruments may be used provided FASP QC criteria are met.

Integrator:	A portable or lap-top computer equipped with the SEFA's PC program will integrate sample spectrograms and data reduction.
Simplifier:	The value of simplifier gain influences the energy calibration of the MCA. The optional setting is usually 1105. This setting may vary for different instruments.
Detector Voltage:	The range is commonly 500 to 1,000 or more volts. Optimum operating conditions occur at 501 volts.
XRF Analysis Time:	A quantitative analysis time of 300 to 500 seconds (live time) is used depending on matrix effects and sample compounds. An analysis time of 20 to 50 seconds may be initially used to screen samples.

4.2 OTHER LABORATORY EQUIPMENT

Other laboratory equipment that will be required for metal analysis in on-site soil and sediment include the following:

1) Polyethylene Sample Cups: 1.25-inch (30-mm) diameter.

2) Mylar Window Film: 0.25-mm thick a higher grade Kapton window film can be used if Mylar is not available.

3) Balance: top load, capable of weighing to 0.01 g, used to weigh samples if drying is required.

4) Drying Oven: either standard convection laboratory oven, or microwave oven for samples that require drying due to excess moisture.

TABLE 4-1

SYSTEM SPECIFICATIONS

Component	Description
SILI X-RAY DETECTOR:	
Guaranteed Resolution:	170 electron volts (eV), (FWHM); 1,000 (cps)
Diameter:	10 millimeters (mm_2)
Active Area:	45 mm^2
Dewar:	.85 liter (L)
Dewar Holding Time:	24 hours (hr)
SAMPLE CHAMBER:	Manual sample selection has a sample access port, four-position sample wheel, and three-position source chamber.
RADIATION SAFETY FEATURES:	Interlocked sample chamber lid prevents accidental exposure to radiation. External exposure is less than .25 [ppMr] (Mr) per hr, 5 centimeters (cm) from unit with sample access door open or closed classified American National Standards Institute (ANSI)-32-985-985-R3.

Radiation Sources	Excitation Energy (keV)	Identification (K) Energies	(L) Energies
Fe-55	5.9	(Al-V)	
Cd-109	22.1	(Tl-Mo)	Barium-Uranium (Ba-U)
Am-241	59.4	(Ga-Tm)	(Pt-U)

MCA SPECTROSCOPY AMPLIFIER	
Gain Ratio:	1 to 16,383
Pulse Shaping:	6 microseconds
Active Baseline Restoration	
Selectable Pulse Pileup Rejector	

TABLE 4-1

SYSTEM SPECIFICATIONS (continued)

(ADC)	
Conversion Rate:	100 megahertz (MHz) Wilkinson type
Gain:	4096, 2048, 1024, 512 channel full scale
Integral Non-Linearity	Plus or minus (±) .025 percent (%) over top 99% full scale
Differential Non-Linearity:	± 1% over top 99% full scale
Detector High Voltage Power Supply Range:	0 to 1000 volts
DATA ACQUISITION AND CONTROL	
Count Capacity:	16,777,215 per channel
Presets:	Live time, count-in channel, integral of (ROI), net counts in ROI
CATHODE RAY TUBE (CRT) DISPLAY	
	7 cm linear and log spectrum
Control:	Expansion, roll, cursor, on, off
Resolution:	2048 x 256 fully-buffered (LCD) Display
KEYBOARD	24 Keys with Positive Tactile Feedback
PROCESSOR	
Memory and Analysis	
Main Memory:	16 kilobytes (Kb), CMOS, SRAM, 56 Kb CMOS, PROM
Data Channels:	4096, 4028, 1024, or 512
Data Analysis:	Overlap, ROI integrals, net area, spectrum shift, energy calibration, automatic peak search
Cassette:	Mini-data cassette
Cassette Format:	Spectrum identification, instrument parameters
Data Time:	40 seconds for 4906 channel spectrum
Cassette Capacity:	10 spectra per cassette
RS-232-C Serial interface to personal computer (PC)	
Maximum Baud Rate:	19.2 Kb
MULTICHANNEL SCALER	
Court Rate:	100 Kb counts per seconds
BATTERY	
12 Volt Rechargeable Battery	12 (VDC)

5.0 _____ insert title please

The following sections provide information on reagents, check standard(s), and matrix spikes. The guidelines presented below will help produce accurate sample analysis results. Calibration techniques are discussed in section 8.0.

5.1 REAGENTS

No reagents are required to prepare sampling for analysis of soils or sediments by the metal analysis method of this FASP.

5.2 CHECK STANDARD(S)

Check standard(s) are calibration standard(s) distinct from those used in the calibration process. These standards are intended for use as an independent check on instrument calibration.

5.3 MATRIX SPIKES

Sample matrix spikes may be prepared by adding element-oxide powders to the sample powder at concentrations required to provide a final sample spike level within FASP QC limits.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples should be collected, handled, preserved, and shipped in accordance with the chain-of-custody requirements complying with current U.S. Environmental Protection Agency (EPA) regulations and recommendations in force at the time of sample collection. The sole exceptions to this rule apply to the sample volumes required by the laboratory. Soil samples should be shipped in 8-ounce, wide-mouthed, glass jars with Teflon-lined caps.

The use of chain-of-custody records described in the EPA "CLP Users Guide" (9240.0-1), December 1988, is required for sample tracking. No holding times have been established for metals analyses of soil or sediment samples.

7.0 CALIBRATION

Stock standard materials or analytes should be manufacturer certified materials, such as Standard Reference Materials from the National Institute of Standards and Technology. It is recommended that standard materials be used with sample materials having consistent matrices. The following sections present initial, continuing, and final calibration procedures.

7.1 INITIAL CALIBRATION

After an experienced x-ray technician has ensured that the entire chromatographic system is functioning properly (that is, that resolution, response reporting, interpretation of x-ray spectra are within acceptable QC limits), the x-ray fluorescence system may be calibrated (see section 10.0). Using at least three calibration standards for each target analyte prepared (as described in Section 5.10), initial calibration curves (such as response versus surface area of standard) are generated for each elemental target compound.

The percent relative standard deviation (%RSD) based on each target compounds calibration factors (CF) computed to determine the acceptability (linearity) of the curve. Unless otherwise specified the %RSD must be less than or equal to 25% or else the calibration is invalid and must be repeated.

7.2 CONTINUING CALIBRATION

The x-ray fluorescence system is rechecked on a regular basis by continuing calibration. The midrange initial calibration standard is generally the most appropriate choice for continuing calibration validation. This single point analysis follows the same analytical procedures used in the initial calibration. Instrument response is used to compute the CF, which is then compared to the mean initial CF and a relative percent difference (RPD) is calculated. Unless otherwise specified, the RPD must be $\leq$ 25% for the continuing calibration to be considered valid. Otherwise, the calibration must be repeated. A continuing calibration remains valid for a maximum of 24 hr, providing the system remains unaltered during that time.

The continuing calibration method is used in all target compound sample concentration calculations for the period over which the calibration has been validated.

7.3 FINAL CALIBRATION

The final calibration must be performed after each batch of samples have been analyzed. The maximum allowable RPD between the mean initial calibration and the final calibration factors for each analyte must be ≤ 50%. A final calibration that achieves ≤ 25% RPD may be used as an ongoing continuing calibration.

8.0 SAMPLE PREPARATION

X-ray fluorescence normally requires very little sample preparation. Most of the time, an adequate quantitative analysis can be obtained by simply placing the sample in a cup or directly in the sample tray. However, optimum accuracy is obtained from samples that are:

- Flat
- Smooth
- Homogeneous
- Infinitely thick
- Dry
- Inorganic

Actual samples rarely meet all of these requirements, so it is necessary to understand the effect of not meeting one or more of these criteria and tailor the analytical strategy accordingly.

If soil or sediment samples contain excess moisture, they should be dried evenly before analysis to minimize the matrix effect of moisture.

No sample extraction or cleanup is required for x-ray fluorescent analysis of soil.

8.1 SPECTROGRAMS

Computer reproductions of spectrograms attenuated to ensure all peaks of metals of interest are optimally displayed for visual identification are acceptable.

The following information must be recorded on each spectrogram.

1) Instrument and detector identification
2) Source identification (Fe-55, Cd-109 or Am-241)
3) Site name
4) Sample number

5) Date and time
6) X-ray fluorescence operator initials

8.2 IDENTIFICATION OF COMPOUNDS

Qualitative identification of analyte compounds is obtained from measuring the energy of the x-rays with the SiLi detector. Each element emits x-rays of characteristic energy when exposed to a source emitting x-rays of higher energy than the inner electron binding energy of the analyte compounds. Quantitative information is provided by comparing the intensity of the characteristic x-rays with standards having known concentrations.

Interferences may preclude positive identification of an analyte compound. In such cases, the analysts should report the presence of the interferents with the maximum possible analyte concentration.

8.3 REGION-SPECIFIC INSTRUMENT PARAMETERS

Specific instrument operating parameters are provided in Appendix A of this FASP SOG.

8.4 ANALYTICAL SEQUENCE

The following steps must be followed in order to analyze target compounds.

1) Instrument blank.
2) Initial calibration.
3) Check standard solution and/or performance evaluation sample (if available).
4) Continuing calibration; repeat within 24 hrs of previous continuing calibration.
5) Associated QC lot method blank.
6) Twenty samples and associated QC lot spike and duplicate.
7) Repeat sequence beginning at 5 until all sample analyses are complete or another continuing calibration is required.
8) Conduct a final calibration when all sample analyses are complete.

9.0 CALCULATIONS

9.1 INITIAL CALIBRATION

SiLi detector response to target compounds is measured by determining CFs. Calculate the CF for each target compound in the initial standard. The integrator may be used to make all of these computations.

$$CF = \frac{\text{Area of Peak}}{\text{Mass of analyte compound in parts per million}}$$

Using the CFs, calculate the %RSD for each target analyte compound at a minimum of three concentration levels using the following equation.

$$\% \text{ RSD} = \frac{SD}{\bar{X}} \times 100$$

where the Standard Deviation (SD), is given by

$$SD = \sum_{i=1}^{\bar{N}} \frac{(X_i - \bar{X})}{N-1}$$

where: X_i = individual CF (per compound)
$\bar{X}$ = mean of initial three CFs (per compound)
N = number of calibration standards.
i =

The %RSD must be ≤ 25%.

9.2 CONTINUING CALIBRATION

Sample quantitation is based on analyte compound CFs calculated from continuing calibrations. Midrange standards for all initial calibration target analyte compounds must be analyzed at specified intervals (≤ 24 hrs).

The maximum allowable RPD calculated using the equation below for each compound must be ≤ 25%.

$$RPD = \frac{|CF_I - CF_C|}{[CF_I - CF_C]/2} \times 100$$

where: CF_I = mean CF from the initial calibration for each compound
CF_C = measured CF from the continuing calibration for the same compound

9.3 FINAL CALIBRATION

The final calibration is obtained at the end of each batch of samples analyzed.

The maximum allowable RPD between the mean initial calibration and final calibration factors for each target compound must be ≤ 50%. A final calibration that achieves ≤ 25% RPD may be used as an ongoing continuing calibration.

$$RPD = \frac{|CF_I - CF_F|}{\frac{CF_I + CF_F}{2}} \times 100$$

where: CF_I = mean CF from the initial calibration for each analyte compound
CF_F = final CF for the same analyte compound

9.4 SAMPLE QUANTITATION

Calculate the compound concentration of the sample with the following equation for external standards. The response can be measured by automated peak height or peak area measurements from an integrator. Sample quantitation is based on analyte calibration factors calculated from continuing calibrations.

$$\text{Concentration } (\mu g/kg) \text{ (wet weight)} = \frac{(A_x)}{(CF_c)}$$

where: A_x = response for the analyte compound to be measured

CF_c = CF from the continuing calibration for the same analyte compound

Report results in (µg/kg) without correction for blank, spike recovery, and percent moisture.

Sample spectra may not identically match with those of analytical standards. When positive identification is questionable, the chemist may calculate and report a maximum possible concentration (flagged as less than the numerical value) that allows data user to determine if additional (for example, CLP RAS or SAS) analytical work is required, or if the reported concentration is below action levels, project objectives, and data quality objectives (DQO) have been met, to forego further analysis.

Similarly, when sample concentration exceeds the linear range, the analyst may report a probable minimum level (flagged as less than the numerical value) that allows the data user to determine if additional (for example, CLP RAS or SAS) analytical work is required, or if the reported concentration is above action levels, project objectives, and DQOs have been met, to forego further analysis.

QC criteria (as described in FASP QC SOGs) must be met for all analyses. Advisory limits for spike percent recovery (%R) and duplicate RPD are presented in Table 9-1.

10.0 EXAMPLE X-RAY FLORESCENCE SPECTRA

The following spectrogram for metal compounds is an example of an x-ray fluorescence spectra for several commonly encountered metals.

TABLE 9-1

FASP MATRIX SPIKE %R AND DUPLICATE RPD ADVISORY LIMITS

Analyte Compound	FASP Advisory QC Limits[a]	
	Spike %R (%)	Duplicate RPD (%)
Antimony	30 to 200	± 100
Arsenic	30 to 200	± 100
Barium	30 to 200	± 100
Cadmium	30 to 200	± 100
Cobalt	30 to 200	± 100
Copper	30 to 200	± 100
Lead	30 to 200	± 100
Chromium	30 to 200	± 100
Mercury	30 to 200	± 100
Nickel	30 to 200	± 100
Selenium	30 to 200	± 100
Silver	30 to 200	± 100
Thallium		
Thorium		
Vanadium	30 to 200	± 100
Zinc	30 to 200	± 100

[a] If the concentration of an FTCL analyte compound is less than five times the FQL, FASP advisory control limits for duplicate RPD values become ±3 times the FQL for that individual analyte compound.

TABLE 11-1

SOIL MATRIX SPIKE %R

Metal	Number of Samples	Mean %R (%)	SD of %R (%)
Antimony			
Arsenic			
Barium			
Cadmium			
Cobalt	[Table to be completed as data becomes available]		
Copper			
Lead			
Chromium			
Mercury			
Nickel			
Selenium			
Silver			
Thallium			
Thorium			
Vanadium			
Zinc			

TABLE 11-2

SOIL TRIPLICATE SAMPLE PRECISION

Metal	Number of Triplicate Sample Groups	Mean %RSD (%)
Antimony		
Arsenic		
Barium		
Cadmium		
Cobalt		
Copper		
Lead	[Table to be completed as data becomes available]	
Chromium		
Mercury		
Nickel		
Selenium		
Silver		
Thallium		
Thorium		
Vanadium		
Zinc		

TABLE 11-3

STATISTICAL COMPARISON OF FASP/CLP METHOD SPLIT SAMPLE ANALYSES

Metal	Number of Samples	Linear Regression Coefficient
Antimony		
Arsenic		
Barium		
Cadmium		
Cobalt		
Copper		
Lead		
Chromium	[Table to be completed as data becomes available]	
Mercury		
Nickel		
Selenium		
Silver		
Thallium		
Thorium		
Vanadium		
Zinc		

11.0 EXAMPLES OF QUALITY ASSURANCE (QA)/QC RESULTS

Spike triplicate and split sample results are presented as examples of FASP empirical data in Tables 11-1, 11-2, and 11-3, respectively.

12.0 DELIVERABLES

FASP deliverables include summaries of sample results and the final FASP report.

12.1 SUMMARIES OF SAMPLE RESULTS

A verbal summary of sample results should be made within 24 hrs of sample analysis by the laboratory. A facsimile type hard copy transmitted by telecommunication may be substituted. If computer compatibility can be established, a modem link may be used to transfer data from the laboratory to field personnel.

12.2 FINAL FASP REPORT

The final FASP report generated for each project should include the following information:

1) A reference to the FASP method used must be made and a note addressing any changes to the method must be included.

2) A hard copy of all data and summary sheets documenting required QA/QC data must be available within 14 days of completion of all FASP analyses for a project.

3) A data summary of all reportable results must be included with units clearly specified.

4) All calculations using standard good measurement practices must be used to determine significant figures. Rounding off numbers will be allowed only for final deliverable values.

5) All sample results will be reported to two significant figures. QC data will be reported to three significant figures.

6) The analyst must submit a statement that initial, continuing, and final CFs, %RSDs, and RPDs meet FASP QC criteria.

7) A summary table of the blank, matrix spike, and duplicate results for each target analyte compound must be included.

8) A summary of FQLs for each target analyte compound is also a final deliverable requirement.

9) A comparison of interlaboratory split sample results should be submitted as an addendum to the final FASP report.

All results must be annotated by the flag, F, by the laboratory to indicate to future data users that FASP techniques were used in sample analyses. For an example of standard reporting format for an example final FASP report, see appendix B.

13.0 SAMPLE AND DATA STORAGE

The following sections discuss disposal of samples, raw and summary data storage, and permanent data storage.

13.1 DISPOSAL OF SAMPLES

Samples should be disposed of in accordance with established federal, state, and local regulations and policies after a minimum holding period of 14 days after receipt by the laboratory.

13.2 RAW AND SUMMARY DATA STORAGE

The lab must maintain a hard copy or computer disk with all raw (including instrument printouts and logbooks) and summary data associated with an analytical case stored on it for a minimum of 6 months after receipt of the hard copy report by the data user.

13.3 PERMANENT DATA STORAGE

After the 6-month period has elapsed, the laboratory should place all records, including laboratory notebooks, into permanent storage files.

REFERENCES

HNU Systems, Inc. (HNU), 1990, Source Excited Fluorescence Analyzer - Portable (SEFA-P, XRF) Operator's Manual, Version 1.0, HNU, Newton, MA.

Jacobuns, N.C., and Driscoll, J.N., 1989, Environmental Applications of an Energy Dispersive X-Ray Fluorescence Analyzer; Presented at the 1989 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlanta, Georgia, March 1989.

November 1991

APPENDIX A

REGION SPECIFIC INSTRUMENT PARAMETERS

METALS ANALYSIS BY X-RAY FLUORESCENCE

(To be added as required by each Region.)

November 1991

APPENDIX B

EXAMPLE FINAL FASP REPORT

METALS ANALYSIS BY X-RAY FLUORESCENCE

November 1991

FASP METALS ANALYSIS BY X-RAY FLUORESCENCE ANALYTICAL RESULTS

SMITH SALVAGE
JONES, OREGON

Report Date: May 1999

DISCLAIMER

This report has been prepared by PRC Environmental Management, Inc. (PRC). Mention of commercial products does not constitute endorsement by PRC. Editing and technical content of this report are the responsibility of PRC.

1.0 INTRODUCTION

Analysis of ten soil samples collected at the Smith Salvage site were made by PRC Environmental Management, Inc. (PRC), analysts, utilizing the FASP mobile laboratory on site. The samples were analyzed for metals by x-ray fluorescence to acquire analytical data as an integral part of an RCRA facility assessment (RFA) sampling visit. Three quality control (QC) samples were also analyzed to monitor analytical method performance and to ensure data validity.

Samples were analyzed using the Standard Operating Guidelines (SOG) for the Field Analytical Support Project (FASP). As required by the U.S. Environmental Protection Agency (EPA), FASP data are annotated with the data qualifier "F," to indicate that FASP methodologies were used to generate the data. As such, qualitative data are defined as tentatively identified and quantitative data should be interpreted as estimated quantities.

Samples were analyzed for the following metals:

Antimony	Mercury
Arsenic	Nickel
Barium	Selenium
Cadmium	Silver
Cobalt	Thallium
Copper	Thorium
Lead	Vanadium
Chromium	Zinc

The samples were collected on April 12, 1999, and received by the laboratory on April 14, 1999. All analyses were completed by April 17, 1999.

2.0 FASP METHODOLOGY FOR METALS BY X-RAY FLUORESCENCE

All samples were analyzed as described in the FASP method for metals analysis by x-ray fluorescence. All FASP method x-ray fluorescence criteria were met for initial calibration, continuing calibration, final calibration, and quantitation limits.

3.0 FASP DATA

FASP data are not confirmed by mass spectroscopy and, therefore, do not provide the same level of qualitative specificity as (CLP) data. FASP data is not equivalent to or a replacement for CLP data, but the results presented in this report are consistent (all samples were

extracted and analyzed by the same procedure). Data generated by PRC for the Smith Salvage site (SSI) were used to quantitate site contamination. The FASP analytical quantitation limits used are presented in Table 3-1.

3.1 METALS SAMPLE ANALYSIS RESULTS

Table 3-2 presents FASP results for metals samples in soil taken from the Smith Salvage site in Jones, Oregon.

3.2 METALS QC DATA

1) Method Blank Results

Table 3-3 presents FASP QC data for sample blanks (in soil) made for the Smith Salvate site in Jones, Oregon.

2) Matrix Spike Results

Table 3-4 presents FASP QC data for metal matrix spike samples in soil taken from the Smith Salvage site in Jones, Oregon.

3) Duplicate Results

Table 3-5 presents FASP QC data for sample duplicates in soil taken from the Smith Salvage site in Jones, Oregon.

TABLE 3-1

(_____) **Fill in title please!**

Metal Analyte	FASP Quantitation Limits (FQL) (micrograms per kilogram - µg/kg)
Antimony	
Arsenic	
Barium	
Cadmium	
Cobalt	
Copper	
Lead	
Chromium	[Table to be completed as data becomes available]
Mercury	
Nickel	
Selenium	
Silver	
Thallium	
Thorium	
Vanadium	
Zinc	

TABLE 3-2

SAMPLE RESULTS
METAL ANALYSIS IN SOIL BY X-RAY FLUORESCENCE
(µg/kg - wet weight)

Metal Analyte	Sample Identification Number									
	JHB-1	JHB-2	JHB-3	JHB-4	JHB-5	JHB-6	JHB-7	JHB-8	JHB-9	JHB-10
Antimony										
Arsenic										
Barium										
Cadmium										
Cobalt										
Copper										
Lead										
Chromium										
Mercury			[Table to be completed as data becomes available]							
Nickel										
Selenium										
Silver										
Thallium										
Thorium										
Vanadium										
Zinc										

U - The metal was analyzed for, but not detected. The associated numerical value is an FQL adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analyte metals are tentatively identified and concentrations are quantitative estimates.

QC data for this group of samples includes:

Blank = MB-1
Spike = JHB-5
Duplicate = JHB-7

TABLE 3-3

METHOD BLANK RESULTS, SOIL
METALS ANALYSIS BY X-RAY FLUORESCENCE
SMITH SALVAGE SITE IN JONES, OREGON
(µg/kg, wet weight)

Metal Analyte	Method Blank - Soil
Antimony	
Arsenic	
Barium	
Cadmium	
Cobalt	
Copper	
Lead	
Chromium	[Table to be completed as data becomes available]
Mercury	
Nickel	
Selenium	
Silver	
Thallium	
Thorium	
Vanadium	
Zinc	

U - The metal was analyzed for but not detected. The associated numerical value is an FQL, adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analyte metals are tentatively identified and concentrations are quantitative estimates.

TABLE 3-4

MATRIX SPIKE RECOVERY RESULTS, SOIL
TOTAL METALS ANALYSIS BY X-RAY FLUORESCENCE
SMITH SALVAGE SITE IN JONES, OREGON
(µg/kg, wet weight)

Metal Analyte	Amount Spiked	Sample	Sample with Spike	Percent Recovery %R)
Antimony				
Arsenic				
Barium				
Cadmium				
Cobalt				
Copper				
Lead				
Chromium	[Table to be completed as data becomes available]			
Mercury				
Nickel				
Selenium				
Silver				
Thallium				
Thorium				
Vanadium				
Zinc				

U - The metal was analyzed for but not detected. The associated numerical value is an FQL adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analyte metals are tentatively identified and concentrations are quantitative estimates.

TABLE 3-5

DUPLICATE RESULTS, SOIL
METALS FASP ANALYSIS
SMITH SALVAGE SITE IN JONES, OREGON
(µg/kg, wet weight)

Metal Analyte	Sample Result	Duplicate Result	Relative Percent Difference (RPD)
Antimony			
Arsenic			
Barium			
Cadmium			
Cobalt			
Copper			
Lead			
Chromium	[Table to be completed as data becomes available]		
Mercury			
Nickel			
Selenium			
Silver			
Thallium			
Thorium			
Vanadium			
Zinc			

U - The metal was analyzed for but not detected. The associated numerical value is an FQL adjusted for sample weight, extract volume, and sample dilution.

F - Data has been generated using FASP methodologies. Analyte metals are tentatively identified and concentrations are quantitative estimates.

4.1.2 MAJOR SYSTEM COMPONENTS

Figure 4-1 shows a front view of the SEFA-P XRF. Main cabinet major components described here include the sample chamber, radioactive source(s), Si(Li) detector, spectrometer electronics, Multichannel Analyzer, battery charger, interlock, digital cassette recorder, and RS-232-C interface.

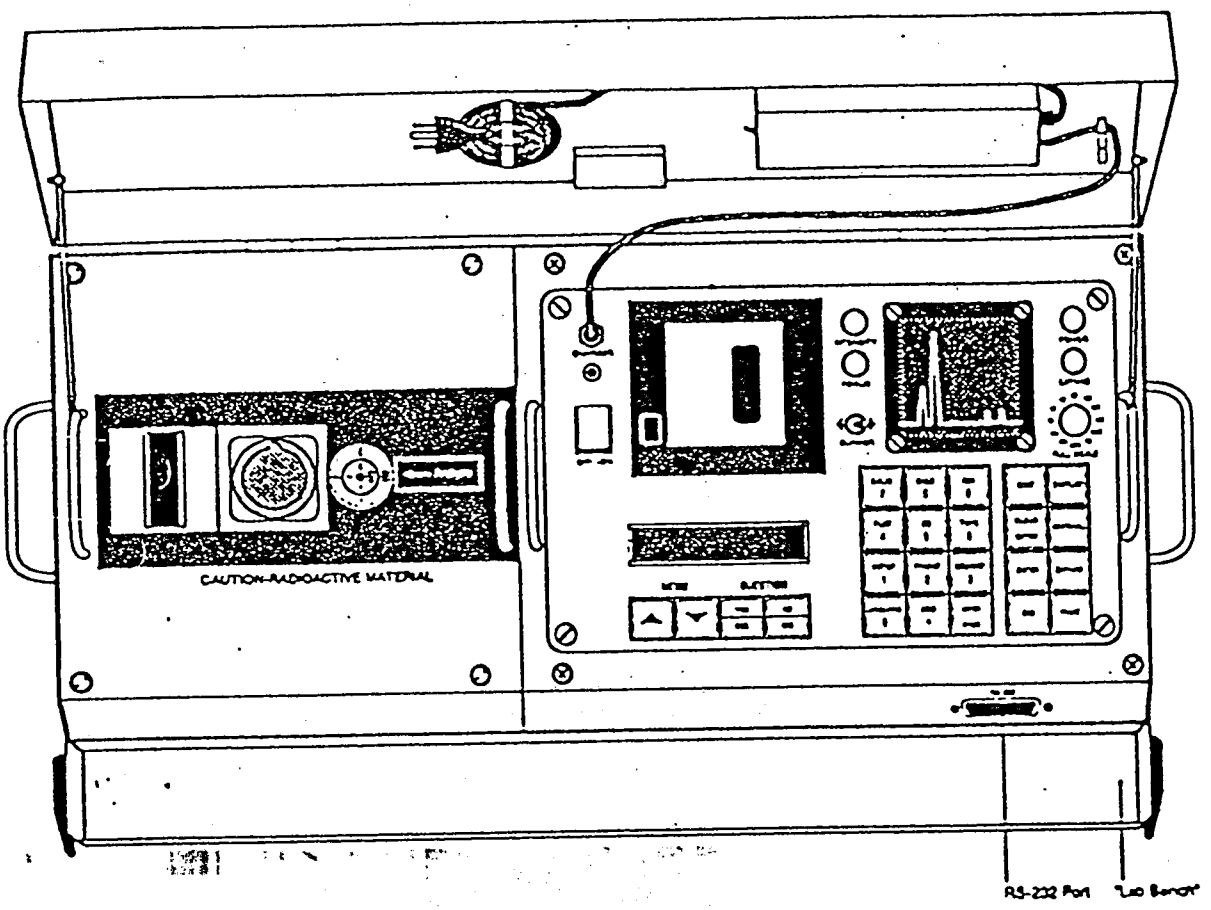

Fig. 4-1 SEFA-P XRF Analyzer Front View

Main Cabinet

A. Interlock/Sample Chamber

A mechanical interlock on the sample changer door is a safety feature that protects the operator from being accidentally exposed to radiation from any of the internal radiation sources. The maximum radiation that emanates from this enclosure is at such a low level that it should not represent a safety hazard. Access to the sample changer is obtained by rotating the source knob to the Safety position, thus allowing the chamber door to be slid open. The door to the sample chamber must be closed to enable operation of the knob that controls selection of the radiation source.

Each installed source is identified by a label on the source knob. The knob that selects the radiation source is marked for four settings; ▲I▲, 1,2, and 3. These settings correspond to Safe, ▲I▲; a detent aids in the proper setting for each source selection. The knob must be set at ▲I▲ to unlatch the chamber door, and the knob cannot be turned to any of the source selections while the chamber is open. When the chamber is closed, the knob can be rotated to expose the contents of the chamber to the selected radiation source.

The sample chamber accommodates four samples at a time. The chamber can be opened (when the source is shielded from the operator) to permit the samples to be inserted or removed.

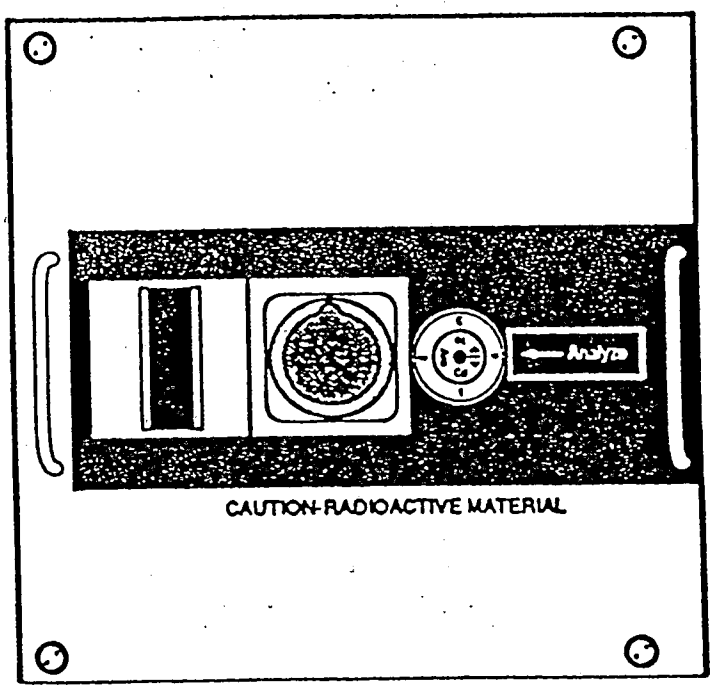

Fig. 4-2 Sample Chamber

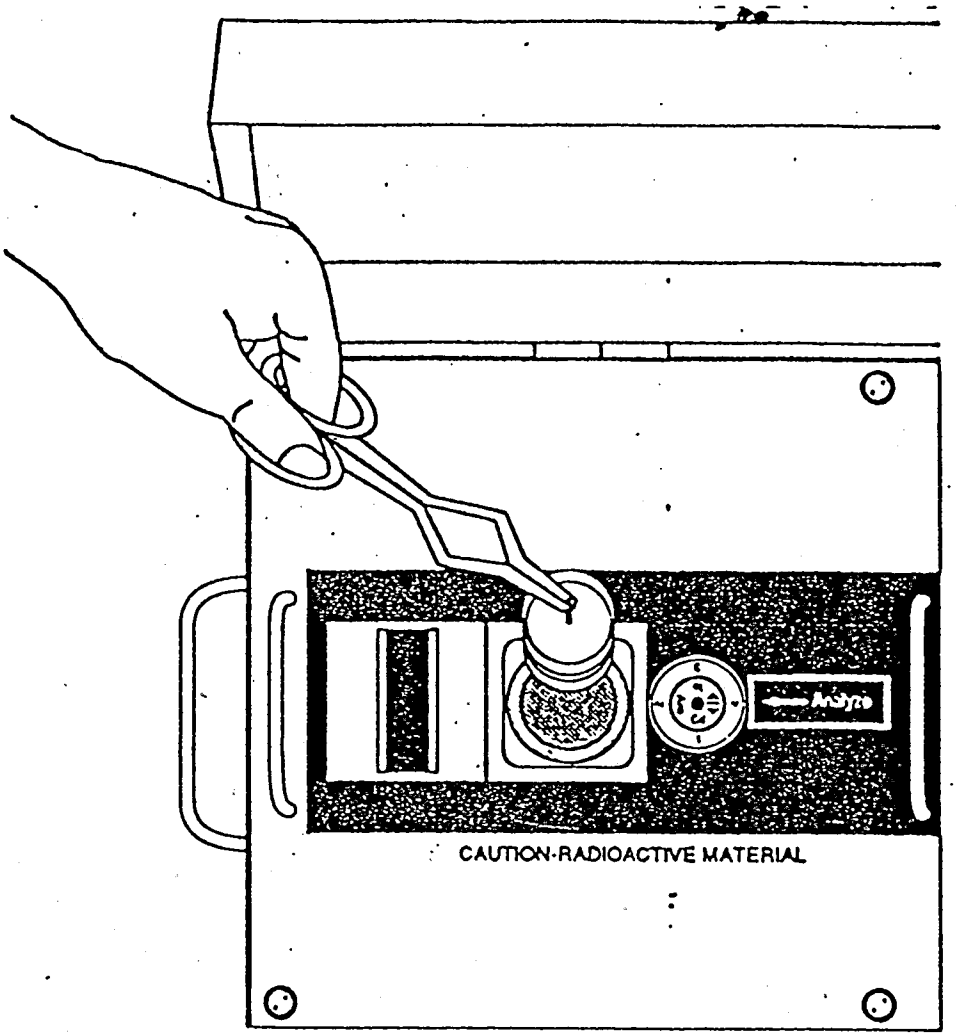

Fig. 4-3 Inserting a Sample Into the Sample Chamber

B. Radioactive Source(s)

The radioactive source causes the sample to ionize the appropriate shell of the analytes present. These three sources are offered with the SEFA-P XRF Analyzer:

Isotope	Maximum Activity
Cd 109	10 mCi
Fe 55	50 mCi
Am 241	25 mCi

10.0 CALCULATIONS

10.1 INITIAL CALIBRATION

Si(Li) detector response to target analytes is measured by determining Calibration Factors (CFs). Calculate the CF for each target analyte in the initial standard. The integrator may be used to make all of these computations.

$$CF = \frac{\text{Area of Peak}}{\text{Mass of Analyte in parts per million}}$$

Using the calibration factors, calculate the percent relative standard deviation (%RSD) for each target analyte at a minimum of three concentration levels using the following equation.

$$\%\ RSD = \frac{SD}{\overline{X}} \times 100$$

where SD. the Standard Deviation, is given by

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(X_i - \overline{X})^2}{N-1}}$$

where: X_i = individual calibration factor (per analyte),
$\overline{X}$ = mean of initial three calibration factors (per analyte),
N = number of calibration standards.

The %RSD must be ≤ 25.0 percent.

10.2 CONTINUING CALIBRATION

Sample quantitation is based on analyte calibration factors calculated from continuing calibrations. Midrange standards for all initial calibration target analytes must be analyzed at specified intervals (≤ 24 hours).

The maximum allowable relative percent difference (RPD) calculated using the equation below for each analyte must be ≤ 25 percent.

$$RPD = \frac{|\overline{CF_I} - CF_C|}{[CF_I - CF_C]/2} \times 100$$

where: $\overline{CF_I}$ = mean CF from the initial calibration for each analyte
CF_C = measured CF from the continuing calibration for the same analyte

10.3 FINAL CALIBRATION

The final calibration is obtained at the end of any batch of samples analyzed.

The maximum allowable RPD between the mean initial calibration and final calibration factors for each target analyte must be ≤ 50 percent. A final calibration that achieves ≤ 25 percent RPD may be used as an ongoing continuing calibration.

$$RPD = \frac{|\overline{CF_I} - CF_F|}{\frac{\overline{CF_I} + CF_F}{2}} \times 100$$

where: $\overline{CF_I}$ = mean CF from the initial calibration for each analyte
CF_F = final CF for the same analyte

10.4 SAMPLE QUANTITATION

Calculate the concentration in the sample using the following equation for external standards. The response can be measured by automated peak height or peak area measurements from an integrator. Sample quantitation is based on analyte calibration factors calculated from continuing calibrations.

$$\text{Concentration } (\mu g/g) \text{ (Wet weight)} = \frac{(A_x)}{(CF_c)}$$

where: A_x = response for the analyte to be measured

CF_c = CF from the continuing calibration for the same analyte

Report results in micrograms per kilogram (μg/g) without correction for blank, spike recovery, or percent moisture.

Sample spectra may not match identically with those of analytical standards. When positive identification is questionable, the chemist may calculate and report a maximum possible concentration (flagged as < the numerical value) that allows the data user to determine if additional (e.g., CLP RAS or SAS) work is required or--if the reported concentration is below action levels and project objectives and Data Quality Objectives (DQOs) have been met, to forego further analysis.

Similarly, when sample concentration exceeds the linear range, the analyst may report a probable minimum level (flagged as > the numerical value) which allows the data user to determine if additional (e.g., CLP RAS or SAS) work is required, or--if the reported concentration is above action levels and project objectives and DQOs have been met--to forego further analysis.

QC criteria (as described in FASP QC SOGs) must be met for all analyses. Advisory limits for spike %R and duplicate RPD are presented in Table 11-1.

11.0 METHOD PERFORMANCE

The following spectrogram is an example of an XRF spectra for several commonly encountered metals.

11.1 XRF SPECTROGRAM - METAL COMPOUNDS

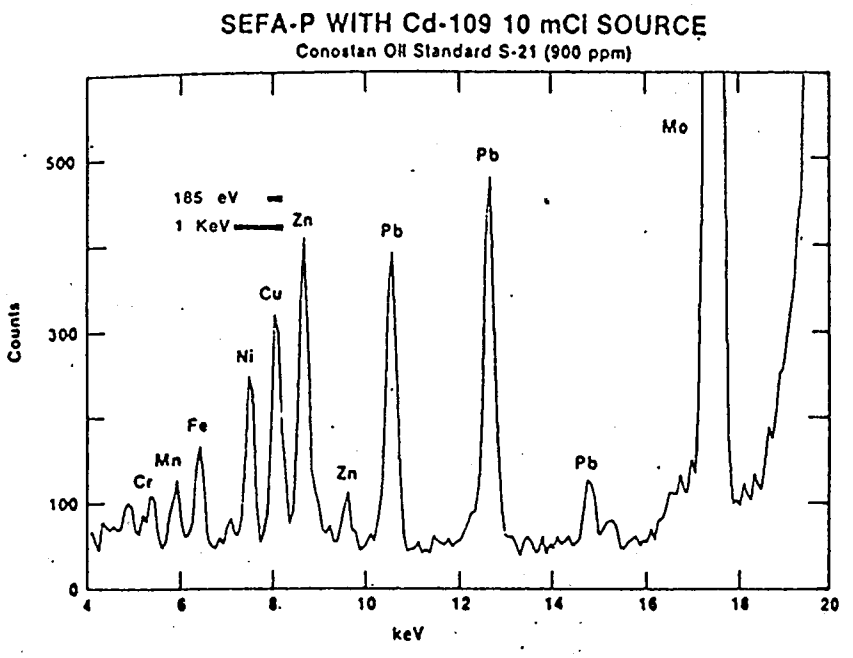

Figure 11-1 Example XRF Spectrum

Source: Cd 109, 10MCi, 22.1 keV

APPENDIX D

ANALYTICAL SERVICES REQUEST FORM

1st Revision

US EPA REGION VII ANALYTICAL SERVICES REQUEST FORM

Activity Number: _____ Date: JANUARY 3, 1992
Site Name, City, & State HYDROCARBON RECYCLERS, WICHITA, KANSAS
EPA Project Leader: MARK MATTHEWS
Section/Branch: PERMITS/RCRA Phone Number: 551-7635
Contractor Contact: ERIC HESS
Contractor: PRC-EMI Phone Number: 281-2277
Projected Sample Delivery Date: JANUARY 13, 1992
Sampling Objective: RFA SAMPLING VISIT

REQUEST SUMMARY

No. of Samples	MGP Code	Matrix	Parameters
8		SOIL	VOA (8240) BNA (8270) METALS (6010) MERCURY (7471)
4 5		WATER	VOA (8240) BNA (8270) METALS (6010) MERCURY (7470)
1		SOIL (TRIP BLK)	VOA (8240)
1		WATER (TRIP BLK)	VOA (8240)

SPECIAL REQUIREMENTS OR COMMENTS

APPROVALS:

Mark T. Matthews 1-3-92
EPA Project Leader (Date)

Lynnell Hamilton 1/3/92
Branch Chief or Section Chief (Date)

DATA REVIEW OPTIONS:

☐ In-Depth (justification req'd.)
☑ Routine

NOTE: SUBMIT TO RQAO/ENSV 30 DAYS PRIOR TO SAMPLE DELIVERY DATE

FOLLOWING TO BE COMPLETED BY ENVIRONMENTAL SERVICES DIVISION ONLY:

Concurrences: ☐ Generic ☐ Site Specific ☐ Other

RQAO _____ Comment: _____

LABO _____

Lab Assignment:
- ☐ Region VII _____
- ☐ CLP _____
- ☐ ESAT _____
- ☐ RECAP _____
- ☐ Other: _____

Scheduled Completion:
- ☐ Routine (In House: 4 weeks) (CLP: 8 weeks)
- ☐ Other: _____

Date: _____

Distribution:
- ☐ EPA Project Leader
- ☐ Chief, LABO/ENSV
- ☐ Chief, GNAN/LABO
- ☐ Chief, ORGN/LABO
- ☐ Chief, CLPM/LABO
- ☐ Data Coordinator
- ☐ RSCC
- ☐ EDSB
- ☐ EMCM
- ☐ EP&R Team Leader
- ☐ ESAT Team Leader
- ☐ Contractor: (above)
- ☐ Other: _____

NOTE: Sampling Supplies Request Form on Other Side

Form Revised 08/23/90